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Short Communication

New approach to synthesis of functionalised silsesquioxanes via hydrosilylation

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ABSTRACT

Synthesis of functionalised silsesquioxanes was carried out in the process of hydrosilylation catalysed by platinum complexes immobilised in ionic liquids. Platinum complexes at different oxidation states in the medium of three ionic liquids. Results of the study indicate that activity of catalytic systems investigated strongly depends on the type of ionic liquid used for metal complex immobilisation as well as on the kind of olefin subjected to hydrosilylation. The most effective catalytic system for all reactions studied was PtCl4 in 1,2,3-trimethylimmidazolium methylsulfate.

1. Introduction

Materials of unique properties, designed for specific functional applications, such as nanocomposites containing nanosized fillers, attracted great interest in recent years [1,2]. Currently, among the most popular nanofillers are polyhedral oligomeric silsequioxanes (POSS) of the general formula $(RSiO_{3/2})_n$, which, due to the presence of organofunctional substituents (R) enable formation of covalent bonds between filler and matrix [3–7]. A particular attention is paid to cage derivatives, especially to those of cubic structure (T_8) [4]. In spite of tremendous application potential of silsesquioxanes, their commercial use is still small, mainly because of high prices of these derivatives which are a result of technologically difficult, time-consuming and low yield methods of their synthesis. This is why a search for new effective methods of synthesis of organofunctional silsesquioxanes is carried out.

A vast majority of the organosilsesquioxanes are prepared by hydrosilylation of an appropriate olefin with hydridosilsesquioxane [4,8,9]. Hydrosilylation is catalysed mainly in homogeneous systems by transition metal complexes, those of platinum in particular [8–10], but unfortunately, isolation of products from post-reaction mixtures often makes a serious problem, particularly in the case of polymeric products of high viscosity or solid products. Therefore efforts are made to apply heterogeneous catalysts or immobilised metal complexes. In recent years, the application of ionic liquids to immobilisation of metal complexes for hydrosilylation processes was reported [11–21], however, biphasic catalysis in a liquid–liquid system was not employed as yet for the synthesis of functionalised silsesquioxanes.

In this paper we report results of research on the application of platinum complexes immobilised in ionic liquids (IL) to synthesis of functionalised silsesquioxanes via hydrosilylation reactions. In these studies, octakis(hydridodimethylsiloxy)octasilsesquioxane (so-called spherosilicate) was used as a reaction substrate.

2. Experimental section

2.1. General methods and chemicals

Octakis(hydridodimethylsiloxy)octasilsesquioxane $(HMe_2SiO)_8[SiO_{1.5}]_8$ was synthesised following published procedures [22]. All olefins and solvents were purchased from Aldrich and used without further purification. Platinum complexes and ionic liquids were purchased from Aldrich and Strem, respectively. All IL were dried prior to use under vacuum at 60 °C for 8 h. The NMR spectra (^1H, ^{13}C, and ^{29}Si) were recorded on Varian Gemini 300 VT and Varian Mercury 300 VT spectrometers. C_6D_6 was used as a solvent. FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases 16 scans at a resolution of 2 cm^{-1} were performed to record the spectra.

2.2. General procedure for catalytic tests

All manipulations were carried out under argon using Schlenk techniques.

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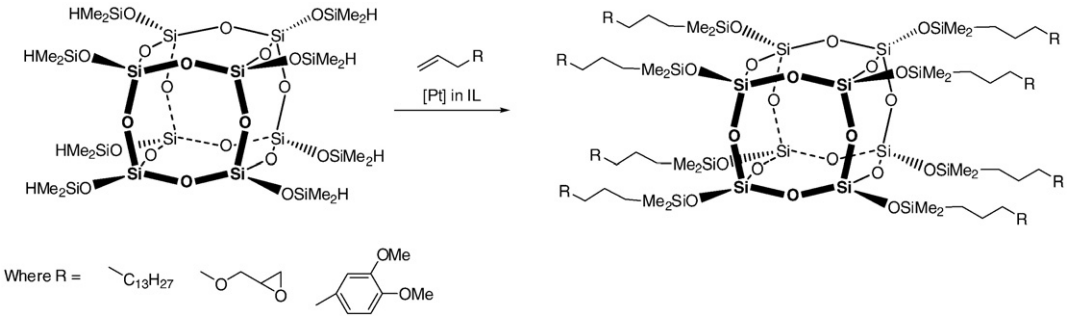


Scheme 1. Model reaction of hydrosilylation of olefins by POSS.

The appropriate amount of a catalyst (in the ratio of 10^{-5} mol per 1 mol Si – H) and the ionic liquid (1% based on total weight of combined substrates) were placed into the reaction vessel and heated to 120 °C for 0.5 h. The system was heated for 0.5 h to dissolve the catalyst in ionic liquid, especially if the ionic liquid was solid at room temperature. Then the reaction system was cooled down and the mixture of octakis(hydridodimethylsiloxy)octasilsesquioxane, 1.2 equiv of olefin (calculated per each Si – H group) and toluene (in the amount indispensable for dissolving silsesquioxane) were added and the reaction vessel was heated again to 120 °C. After 1 h, the reaction vessel was cooled to room temperature and then the reaction mixture was separated from the catalytic system by decantation. The mixture was analysed by FT-IR spectroscopy and then, after the evaporation of toluene, the formation of desired products was verified by NMR analysis. The recovered catalytic system (catalyst in ionic liquid) was reused in the next reaction run.

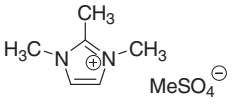
3. Results and discussion

Hydrosilylation was carried out using three olefins: hexadecene, allyl glycidyl ether and 4-allyl-1,2-dimethoxybenzene, as shown in Scheme 1.

The above reactions were catalysed by systems based on four platinum complexes $PtCl_4$, $K_2[PtCl_4]$, $K_2[PtCl_6]$, and $[Pt_2\{(CH_2{=}CHSiMe_2)O\}_3]$ (Karstedt's catalyst).

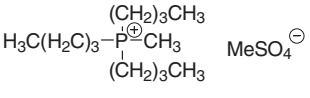
The complexes were immobilised in the following ionic liquids (IL), shown in Figs. 1–3.

Our earlier studies have shown that the effectiveness of a catalytic system for hydrosilylation processes depends on the kind of ionic liquid. The latter should be a good solvent for a metal complex and firmly immobilise the complex while enabling to maintain its high catalytic activity, should form biphasic systems with parent substances and products and should be stable in the presence of reactive parent substances while not interacting with products. All these properties of ionic liquids are affected by the choice of cation and anion present in an ionic liquid. In our earlier studies we employed a dozen of different IL where anions were, among others, halogen ions (Cl^-, Br^-) or fluorine derivatives (BF_4^-, PF_6^-, $SO_3CF_3^-$) [18,19]. However, these liquids appeared to be ineffective due to either poor solubility of metal complexes in them, difficulties in separation of catalytic system from reaction products (most of halogen anion-containing liquids) or drastic decrease in catalytic activity in subsequent reaction runs (fluorine derivatives). In the latter case, one of the reasons for catalyst deactivation is the decomposition of ionic liquid (caused by the access of moisture) and the release of free fluoride ions that poison the catalyst [19]. Despite drying parent materials and ionic liquid prior to reaction, traces of moisture can access the system during isolation of product from catalytic system. On the other hand, we have found that IL that contain SO_2 group in their anion ($MeSO_4^-$, $(CF_3SO_2)_2N^-$, Ace^-, Sac^-) are characterised by good stability and dissolve metal complexes well [20]. This is why the ionic liquids selected for the present study meet the above criteria. However, it has to be added that all our earlier studies on hydrosilylation in the presence of IL were carried out without solvents, but in this study the necessity appeared of using a solvent, because octakis(hydridodimethylsiloxy)octasilsesquioxane is a solid poorly soluble in olefins involved in the reaction. Therefore we applied toluene which dissolves the starting silsesquioxane, and the solution obtained in such a way was mixed with a particular olefin at an appropriate stoichiometric ratio. The mixture of parent materials was added to the catalytic system that was prepared earlier by dissolving a metal complex in an ionic liquid. As it was mentioned earlier, the ionic liquid made 1% based on total weight of combined substrates. Such an amount of ionic liquid secured complete solubility of metal complex and facilitated isolation of reaction product from catalytic system. Too large amount of ionic liquid caused a great dilution of catalyst (that was used at a low concentration of 10^{-5} mol per 1 mol of Si – H), which resulted in slowing down the reaction, whereas too small amount of ionic liquid led to difficulties in accurate separation of reaction products from catalytic system. As already mentioned, the choice of ionic liquids (based on our earlier experience) was performed in such a way that complete solubility of employed metal complexes was secured. To obtain a fully homogeneous system, ionic liquid together with a metal complex was heated at 120 °C for half an hour. After cooling down, the catalytic system formed in such a way was homogeneous and no precipitation of metal complex occurred even after long time of storage. In all cases, the catalytic system did not dissolve in the reaction mixture, therefore the process was performed in a biphasic system and, after the reaction completion, the mixture was decanted and a next portion of reactants was introduced into the catalytic system to continue the process. All reactions were carried out for 1 h followed by FT-IR analysis of the post-reaction mixture (after its separation from the catalytic system) and Si – H conversion was determined on the ground of a decrease in the intensity of the band at about 2100 cm^{-1}. In this way the progress in the reaction carried out in the presence of the same portion of catalyst in subsequent catalytic runs was determined. The formation of a desirable compound was verified



I

Fig. 1. 1,2,3-Trimethylimidazolium methylsulphate [TriMIM][$MeSO_4$] (**I**).



II

Fig. 2. Tributyl(methyl)phosphonium methylsulphate [TriBMP][$MeSO_4$] (**II**).