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Biphasic platinum catalyzed hydrosilylation of terminal alkenes in TAAILs

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Dedicated to Prof. Dr. Wolfgang A. Herrmann on the occasion of his 65th birthday.

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ABSTRACT

A new catalytic system, based on tailored aryl alkyl ionic liquids and commercially available platinum sources, was developed for the hydrosilylation of alkenes in a biphasic mixture, which allows for easy recovery of the expensive metal catalyst. Commercially available platinum compounds were dissolved in recently developed TAAILs (Tunable Aryl Alkyl Ionic Liquids), which allow the reaction to be carried out at 50 °C in air. No inert gas atmosphere is required and no platinum black is observed during the reaction. The biphasic catalysis leads to excellent selectivities and turn-over values as well as full recovery of the catalyst. The catalytic system shows the known chemoselectivity for terminal alkenes.

1. Introduction

The hydrosilylation of alkenes is one of the most important industrial large scale processes [1] and is used for the production of organofunctional silanes [2,3], alkyl silanes [4], vinyl silanes [4] and silicone polymers [5–7]. The generation of alkyl- and vinylsilanes via a hydrosilylation reaction is highly atom-economical [4] and is used in the production of silicon polymers [5–7].

A three-dimensional network results from the crosslinking of multifunctional silicone hybrid polymers with multi-vinyl functional silicone polymers [8,9]. Hybrid polymers can be created via the coupling of silanes and siloxanes with organic polymers using hydrosilylation reactions. These materials are often applied for coatings [10,11]. In organic synthesis silicon containing compounds have achieved great importance in the replacement [12] of highly toxic and environmentally critical boron and tin compounds for transition metal catalyzed coupling reactions [13–17].

Several catalytic systems have been developed, but they generally suffer from catalyst degradation, leaking of the catalyst and contamination of the product with platinum black. Often phosphine based ligands are used, which are sensitive to oxidation and slow the reaction rate, but stabilize the catalyst.

The commonly used “industrial standard catalyst” for the hydrosilylation is the platinum–cyclovinylmethylsiloxane complex (Karstedt catalyst, Fig. 1) [18]. It is very reactive, but has the disadvantage that it decomposes during the reaction forming platinum colloids or platinum black, depending on the solvent used. It also leads to the formation of various unwanted side products (C–F, Scheme 1). For most applications the linear product B with a high selectivity (ratio of A:B) is preferred.

For several years ionic liquids have been investigated as solvents or co-solvents in catalytic reactions. A very broad overview, including structures and properties as well as catalytic applications of ionic liquids is given in an excellent review article [19]. Especially in biphasic catalysis ionic liquids are usually the reaction medium carrying the catalyst [20–22], thereby facilitating the separation of metal catalyst and product. This allows for an easy recovery of the precious metal catalyst and prevents metal contamination of the product. In addition there often is no need for expensive and complicated ligand systems when metal salts can be used as catalysts.

One example for a study where various platinum compounds like $PtCl_2(cod)$, $PtCl_2(PPh_3)_4$, $Pt(PPh_3)_4$, $[PtCl_2(C_6H_{10})]_2$, or K_2PtCl_4 have been used in different pyridinium and imidazolium based ionic liquids as the catalyst phase for catalytic hydrosilylation reactions is the reaction of 1-hexadecene with siloxane B9800. The formation of platinum black from $PtCl_2(cod)$, $[PtCl_2(C_6H_{10})_2]_2$ and K_2PtCl_4 during the reaction is a drawback in this study. An increase

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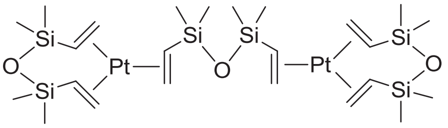


Fig. 1. Structure of the platinum–cyclovinylmethylsiloxane complex (Karstedt catalyst) [18].

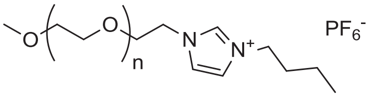


Fig. 2. Structure of [mPEGIm][PF$_6$].

of the reaction temperature from 90 °C to 110 °C leads to higher conversion, but also accelerates the deterioration of the catalytic system [23].

Next to platinum, also other catalytically active precious metals like rhodium, have been tested in the biphasic hydrosilylation of olefins. In 2008 the Wilkinson catalyst Rh(PPh$_3$)$_3$Cl was used along with a poly(ethylene glycol) functionalized ionic liquid ([mPEGIm][PF$_6$], Fig. 2) in the reaction of various alkenes with triethoxysilane [24]. Despite full conversion the catalytic system provided only poor selectivities in favor of the *anti*-Markovnikov product, e.g. 87% for styrene. Further disadvantages are the high reaction temperature of 90 °C as it leads to a lower selectivity and the high catalyst loading of 1000 ppm (0.1 mol%). The selectivity and conversion is even worse in organic solvents (THF and benzene) and 1-butyl-3-methylimidazolium hexafluorophosphate [24].

The development of ionic liquids (ILs) in the last decade has been application driven. While the first generation of ILs had been sensitive toward moisture, exchange of AlCl$_4^-$ against other counter ions like PF$_6^-$ or BF$_4^-$ lead to the next generation of ILs. The following generation was then termed TSILs (task specific ionic liquids) which carried functional groups or heteroatoms in the chain. Different organic cations based on ammonium or phosphonium ions or on heterocycles like pyridinium, pyrrolidinium, triazolium or imidazolium have been developed, leading to a multitude of compounds, mostly based on 1-methylimidazole. But recently we developed a completely new class of ionic liquids [25,26]. These new ionic liquids, termed *TAAILs* (*T*unable *A*ryl *A*lkyl *I*onic *L*iquids), are clearly different from all other ionic liquids (Fig. 4). Standard imidazolium based ionic liquids carry two alkyl chains (Csp^3), which are limited to inductive effects (+I, −I). In contrast, the TAAIL concept introduces mesomeric effects (+M, −M) by having a substituted phenyl ring (Csp^2) instead of one of the alkyl substituents. As in the case of the standard ILs the anions (Fig. 3, A$^-$) can be chosen without restrictions.

Although the dihedral angle between the two rings is not zero, a significant electronic communication could be identified [27]. As the electronic situation of the phenyl ring can be changed by the type (donating/withdrawing), number (0–5) and position (ortho/meta/para) of the substituent on the ring, this new concept opens the door to a multitude of new ionic liquids. We have used this substituent effect to fine tune the solvent properties of our new TAAILs for applications in biphasic catalysis.

The catalyst phase is formed by dissolving the platinum precursor in one of the TAAILs. The reactants are dissolved in petroleum ether, which is immiscible with the ionic liquid, forming the second phase. After completion of the reaction the two phases are separated by decantation and the catalyst phase can be reused without further treatment. Next to this batch mode it is also possible to run the ionic liquid supported biphasic hydrosilylation in a continuous loop reactor [28].

As a model reaction we chose the hydrosilylation of various alkenes with dimethylphenylsilane (Scheme 2).

As platinum sources we used PtCl$_2$ and the Karstedt catalyst (Fig. 1) in combination with four TAAILs and varied the structure of the alkene to check whether our new catalytic system works for aliphatic olefins with different substituents and also for cyclic olefins (Fig. 4).

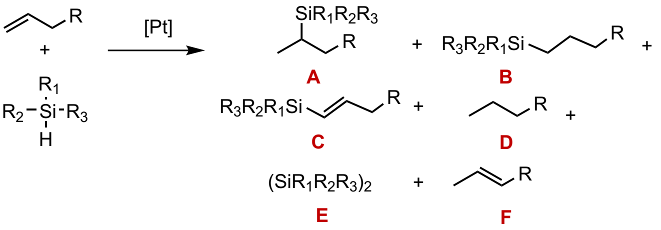
To benchmark our results we used 1-butyl-3-methylimidazolium bis(trifluormethanesulfonyl)-imide ([BMIM][N(Tf)$_2$]) in combination with platinum salts and the Karstedt catalyst (Fig. 1) in petroleum ether without ionic liquid. For this investigation we chose four donor substituted TAAILs as catalyst carriers in the biphasic hydrosilylation of olefins (Scheme 3).

2. Results and discussion

There are several platinum salts commercially available, but due to the number of possible combinations with the different ionic liquids we restricted our study to PtCl$_2$ as an example for a platinum(II) compound and the Karstedt catalyst (Fig. 1) as an example for a well known platinum(0) compound. We recently reported results on the homogenous hydrosilylation with platinum(II)–NHC compounds prepared from Pt(acac)$_2$ and imidazolium salts [29–32]. Using similar imidazolium salts as ionic liquids in the biphasic hydrosilylation the formation of catalytically active platinum species is feasible. The nature and activity of these *in situ* generated catalysts should therefore depend on the structure of the ionic liquid.

For PtCl$_2$ and the Karstedt catalyst we checked the influence of the ionic liquids for different substrates. In Table 1 various TAAIL based catalytic systems with PtCl$_2$ and the Karstedt catalyst are compared for the substrates 1-octene (**a**) and 1-decene (**b**). It turns out that for the hydrosilylation of 1-alkenes platinum chloride is the better platinum source compared to the Karstedt catalyst, showing almost complete conversion for all ionic liquids, even for the standard IL (Table 1). Consequently, there are only small differences between the four different TAAILs with platinum chloride as pre-catalyst.

One possible explanation for the low reactivity of the Karstedt complex in ionic liquids is that the platinum(0) species might react with the imidazolium cations. This could lead to the formation of tetracarbene platinum(II) complexes, which should not be active in the hydrosilylation [33–35]. We could recently also demonstrate



Scheme 1. Possible side products of the hydrosilylation of alkenes.

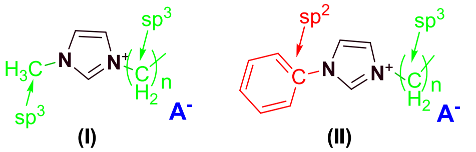


Fig. 3. Comparison of standard imidazolium based ionic liquids (I) and TAAILs (II).