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Liquid-Liquid Biphasic, Platinum-Catalyzed Hydrosilylation of Allyl Chloride with Trichlorosilane using an Ionic Liquid Catalyst Phase in a Continuous Loop Reactor

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Abstract: The platinum-catalyzed hydrosilylation of allyl chloride with trichlorosilane was investigated in an ionic liquid-organic biphasic reaction mode. After an ionic liquid screening and repetitive batch mode experiments, the process was realized in a continuous mode using a loop reactor concept with integrated continuous separation and recycling of the ionic liquid catalyst phase. The continuous reactor could be operated for 48 h at constant activity and selectivity without addition of platinum indicating that platinum leaching into the product phase was far below 1 ppm. Enhanced selectivity for the product trichloro(3-chloropropyl)silane (compared to the state-of-the art) and the possibility to use simple platinum tetrachloride ($PtCl_4$) as platinum source are further attractive features of this new ionic liquid-based process concept.

Keywords: catalyst recycling; hydrosilylation; ionic liquids; multiphase catalysis; platinum

Introduction

Biphasic catalysis in a liquid-liquid system provides a powerful approach to combine the advantages of both homogeneous and heterogeneous catalysis. The reaction mixture consists of two immiscible solvents. Only one phase contains the catalyst, allowing easy product separation and catalyst recycling by simple decantation. However, the right combination of catalyst, catalyst solvent, reactants and products is crucial for the success of biphasic catalysis.[1] The catalyst solvent has to provide excellent solubility and immobilization for the catalyst complex to prevent metal leaching into the product phase under the operating conditions. These solvent characteristics have to be achieved without the solvent competing with the substrate for the free coordination sites at the catalytic centre. Another important precondition is given by the fact that the catalyst solvent should be stable towards feedstock, products and process conditions in order to provide a fully recyclable catalyst solution with a long lifetime.

This latter requirement may sound trivial but it has been the major hurdle to realize successfully liquid-liquid biphasic reactions in many cases, a particular interesting example being transition metal-catalyzed hydrosilylation.

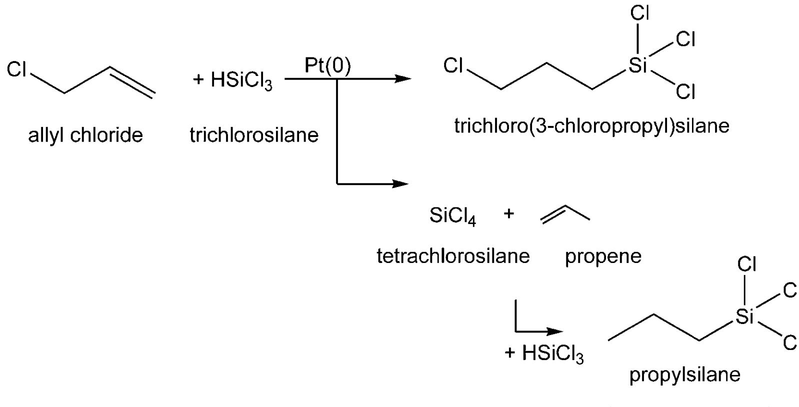
Hydrosilylation represents the metal-catalyzed *anti*-Markovnikov addition of an Si–H moiety to alkenes with formation of a new Si–C bond.[2,3] The mechanism of this reaction has been studied in detail and is known to follow the so-called Chalk–Harrod mechanism[4] with catalyst precursors like chloroplatinic acid being frequently applied.[5,6] The reaction is of high preparative value and has also found extensive use for the technical production of organosilane compounds and organo-modified oligosiloxanes.[7] However, attempts to realize liquid-liquid biphasic hydrosilylation failed in the past due to the reactivity of most Si–H compounds with the polar solvents that might be used to form a biphasic system with the products or an alkane extraction phase. In fact, traditional biphasic solvent mixtures such as, for example, water-alkane or butanediol-alkane are not applicable. As a consequence, in the traditional industrial hydrosilylation processes, the expensive transition metal catalyst remains homogeneously dissolved in the product or is recycled by extensive downstream processing from the high-boiling residues of the product distillation.

Ionic liquids are salts with melting points below 100 °C which have attracted much interest in both academic and industrial research laboratories during the last decade.[8] With respect to applications in multiphase catalysis, this class of innovative liquid materials has shown to offer unique combinations of properties, such as, e. g., the combination of extremely low vapour pressure, low nucleophilicity, high solvation properties and tunable miscibility with common organic solvents.[9]

The field of ionic liquid multiphase hydrosilylation was pioneered by Behr and Toslu in 2000 who investigated the hydrosilylation of 10-undecenoic acid methyl ester with triethoxysilane using the Speier catalyst, $H_2PtCl_6 \cdot 6H_2O$, dissolved in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] [PF_6]).[10] By applying cyclohexane as extraction solvent and by making use of the thermomorphic phase behaviour of the system, these authors were able to demonstrate the feasibility of biphasic catalysis. A successful recycling of the ionic liquid catalyst solution was also demonstrated. An example of Rh-catalyzed hydrosilylation was provided by van Koeten et al. who applied a fluorinated version of Wilkinson's catalyst dissolved in an ionic liquid functionalized with perfluorinated alkyl chains to react 1-octene with dimethylphenylsilane.[11] Initially, the catalyst proved to be more active in the ionic liquid compared to conventional solvents. However, reaction rates went down during recycling and dropped to only 10% activity of the same reaction in benzene in the 15th cycle. The authors could explain this decrease in activity with the detection of Rh and phosphine leaching from the ionic liquid phase (respectively, 4% and 2% per cycle, with regard to the initial added amounts). Another example of Rh-catalyzed hydrosilylation was published in 2006 by Marciniec and co-workers.[12] These authors demonstrated reasonable recyclability of the ionic catalyst solution in a polysiloxane modification reaction *via* hydrosilylation using *N*-alkylpyridinium hexafluorophosphates in Rh-catalyzed hydrosilylation reactions. Lai and co-workers could demonstrate a simple recycling by decantation as the selected supports are liquids under the reaction conditions and solids at room temperature.[13]

A first publication demonstrating the industrial attractiveness of hydrosilylation catalysis in ionic liquids was provided by researchers from Degussa AG (nowadays Evonik Industries).[14] They investigated the reaction of 1-hexadecene with oligosiloxanes using extremely low catalyst loadings in the ionic liquid phase (5 ppm Pt relative to the total mass of substrates) and reached high conversions within affordable reaction times of 60 min. In repetitive batch experiments, total turnover numbers of 1,500,000 could be realized by recycling the ionic catalyst solution over ten cycles. The authors stated the importance to avoid 1,3-dialkylimidazolium ionic liquids for this application as the *in situ* NHC-carbene complex formation appeared to be the reason for low catalyst activity in some systems. With pyridinium tetrafluoroborate, average conversions of $>86\%$ (with K_2PtCl_4) and $>82\%$ [with $PtCl_2(PPh_3)_2$] could be realized.

In the present paper, we studied the feasibility to expand these approaches for ionic liquid-organic biphasic hydrosilylation catalysis to the transformation of chlorosilanes. We investigated the industrially relevant Pt-catalyzed reaction of allyl chloride and trichlorosilane to form trichloro(3-chloropropyl)silane, which is a multi-ton product as additive for polymers and as intermediate for the production of other surface active-organosilanes (Scheme 1).[15] As a matter of fact, this process is technically challenging due to the difficult handling of the highly flammable, volatile, very easily hydrolyzable and chemically aggressive trichlorosilane. Moreover, the reaction shows a complex selectivity pattern. In fact, besides the main reaction leading to desired trichloro(3-chloropropyl)silane, trichlorosilane and allyl chloride can be converted in a side reaction to tetrachlorosilane and propylene. The propylene generated in this way undergoes consecutive hydrosilylation forming trichloropro-



Scheme 1. Hydrosilylation of allyl chloride and trichlorosilane to form trichloro(3-chloropropyl)silane – main reaction and relevant side reactions forming tetrachlorosilane, propene and trichloropropylsilane.

pylsilane. The latter finds no commercial use and constitutes a waste material (Scheme 1). Thus, increasing the selectivity to trichloro(3-chloropropyl)silane in comparison to the actual state-of-the art is an important issue of the process optimization in addition to the aforementioned catalyst immobilization and recycling aspects.

Moreover, in the present paper, we report for the first time an ionic liquid-based hydrosilylation reaction in a continuous reaction mode including continuous separation and recycling of the ionic liquid catalyst phase. The transition from repetitive batch mode operation to a continuous reaction mode is a very important step in the process development since long-term catalyst stability, leaching aspects and productivity issues can be demonstrated much more reliably from a continuous system.

Results and Discussion

Preliminary Ionic Liquid Screening

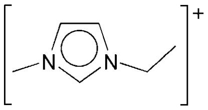
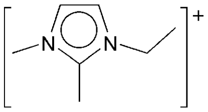
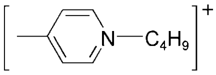
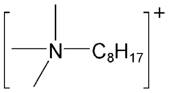
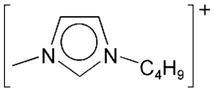
The first important step of our study was to demonstrate that ionic liquids can indeed act as a suitable reaction medium for the Pt-catalyzed hydrosilylation of allyl chloride with trichlorosilane. Initially, we focused our attention on three aspects that were assumed to be of key relevance for the successful realization of the concept, namely: a) sufficient solubility of the envisaged Pt catalyst precursor $PtCl_4$ in the ionic liquid; b) stability of the ionic liquid against the highly reactive trichlorosilane substrate; c) stability of the desired product trichloro(3-chloropropylsilane) in the ionic liquid under operative conditions. These three criteria were applied to screen a number of ionic liquids for their suitability for the hydrosilylation of allylchloride and trichlorosilane.

The ionic liquids selected for the initial screening are depicted in Table 1.

The selected Pt source, $PtCl_4$, was found to be sufficiently soluble in all these ionic liquids under investigation (Pt loading above 4000 ppm as determined by ICP), both at room temperature and at the reaction temperature of 100 °C.

The stability of the ionic liquid against trichlorosilane proved to be a more selective prerequisite for the ionic liquid selection. All ionic liquids have been dried very carefully prior to these stability experiments. Nevertheless, in the ionic liquids [EMIM] [$EtSO_4$], [EMIM] [tosylate] and [BMIM] [BF_4] decomposition was immediate, obviously due to a reaction of the ionic liquid's anion with trichlorosilane even at room temperature. This decomposition process was also obvious from the fact that gaseous products and a solid formed while trichlorosilane was added to the ionic liquid. Also the ionic liquids [EMIM] [Et_2PO_4], [EMIM] [CF_3SO_3] and [BMIM] [PF_6] showed some signs of silane decomposition but to a lesser extent. Importantly, no decomposition of $HSiCl_3$ was observed in all [Tf_2N]-based ionic liquids. Obviously, the strongly electron-withdrawing effect of

Table 1. Ionic liquids used for the initial screening.

Name	Abbreviation	Structure of cation
1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[EMIM] [Tf_2N]	
1-ethyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide	[EMMIM] [Tf_2N]	
1-butyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide	[3-MBPy] [Tf_2N]	
trimethyloctylammonium bis(trifluoromethanesulfonyl)imide	[OMA] [Tf_2N]	
1-ethyl-3-methylimidazolium ethyl sulfate	[EMIM] [$EtSO_4$]	
1-ethyl-3-methylimidazolium diethyl phosphate	[EMIM] [Et_2PO_4]	
1-ethyl-3-methylimidazolium 4-methylbenzenesulfonate	[EMIM] [tosylate]	
1-ethyl-3-methylimidazolium trifluoromethanesulfonate	[EMIM] [CF_3SO_3]	
1-butyl-3-methylimidazolium hexafluorophosphate	[BMIM] [PF_6]	
1-butyl-3-methylimidazolium tetrafluoroborate	[BMIM] [BF_4]	

the two trifluoromethyl groups leads to the fact that the SO_2 groups of the anion become inert against trichlorosilane. Even during prolonged heating (96 h, 120 °C in an autoclave) these $[Tf_2N]^-$-based ionic liquids proved to be stable against $HSiCl_3$.

In order to ascertain the stability of the reaction product in contact with the ionic catalyst solution, a solution of trichloro(3-chloropropyl)silane in the ionic liquid [EMMIM] $[Tf_2N]$ containing 2000 ppm of $PtCl_4$ was heated to 100 °C for 6 h. No transformation of trichloro(3-chloropropyl)silane, for example, by substituent exchange at the Si atom, could be found. This distinguishes the bis(trifluoromethanesulfonyl)imide systems from chloroaluminate ionic liquids for which the ligand exchange reaction at organochlorosilanes has been described in an earlier patent of Wacker Chemie AG.[16]

Experiments in a Semi-Batch Glass Reactor at Atmospheric Pressure

Having identified bis(trifluoromethanesulfonyl)imide ionic liquids as suitable catalyst phases, our first set of experiments was carried out in a semi-batch mode using a glass reactor at atmospheric pressure (for details see Experimental Section).

Table 2 displays the results for selected $[Tf_2N]^-$ ionic liquid systems compared with the homogeneous, industrially applied catalyst system (here denoted as "Wacker catalyst"). The latter is rather unspecified and predominantly consists of a mixture of dimeric Pt species with cylooctadiene as ligands in such an amount to ensure a Pt concentration of about 500 ppm in an organic matrix consisting of mixed saturated hydrocarbons.

Varying the ionic liquid cation resulted in little differences in selectivities and reactivities (Table 2, entries 1–3). In contrast to reports by Dyson et al.,[13] the possibility for *in situ* formation of NHC complexes does not exert a major negative effect on the formation and activity of the catalytic species for this specific reaction. In fact, a potentially NHC-forming ionic liquid cation, such as $[EMIM]^+$, showed similar results compared to a non-NHC-forming cation, such as $[EtPy]^+$.

The comparison of the liquid-liquid biphasic runs (Table 2, entries 1–3) with the homogeneous system applying an original technical catalyst sample provided by Wacker (Table 2, entry 4) was also very instructive. In fact, already the first semi-batch experiments provided a clear indication that – at least for this specific hydrosilylation reaction – the ionic liquid biphasic system leads to a slightly improved selectivity (by 3.0 to 4.6% in S1), a result that could be reproduced many times in the course of our study.

In this context, it is noteworthy that the difference in S1 *vs.* S_{total} selectivity originates from the additional hydrosilylation reaction of the by-product propene. While S1 takes only into account the ratio of allyl chloride hydrosilylation *vs.* chloride transfer, S_{total} is additionally influenced by the consecutive hydrosilylation of propene (formed as the by-product in chloride transfer). Due to the highly volatile nature of the propene, S_{total} values of different experiments can only be properly compared for cases in which the mass balance of all reactants can be fully accounted.

Concerning activity, it is important to note that the turnover frequencies given in Table 2 are not suitable for a proper comparison of catalyst activities as all data were collected at full or almost full conversion. However, the values obtained clearly indicate that also in the case of liquid-liquid biphasic operation very good activities can be achieved even with low catalyst loadings.

Another interesting result from these first semi-batch experiments is the fact that the ionic liquid-based reactions can indeed be successfully carried out

Table 2. Hydrosilylation of allyl chloride with trichlorosilane in a pressure-less semi-batch reaction system: comparison of different solvents and catalyst systems.[a]

Entry	Solvent	Catalyst	Catalyst concentration ppm	Conversion [%]	S_{total}[b] [%]	S1[c] [%]	TOF[d] [h^{-1}]
1	[EMIM] $[Tf_2N]$	$PtCl_4$	600	100	71.7	81.9	1430
2	[EMMIM] $[Tf_2N]$	$PtCl_4$	300	98.4	74.7	80.9	3780
3	[EtPy] $[Tf_2N]$	$PtCl_4$	200	100	74.3	80.3	3280
4	reactants	Wacker catalyst[e]	500	100	70.6	77.3	1180

[a] *Conditions:* catalyst concentration: 200–600 ppm Pt in the solvent, $HSiCl_3$/allyl chloride: 1.25:1.0, T_{start} = 100 °C, reaction time: 20 min, mass balance could be accounted for all experiments within 2%.

[b] S_{total} = mol [(3-chloropropyl)trichlorosilane]/{mol [(3-chloropropyl)trichlorosilane] + mol (tetrachlorosilane) + mol (propyltrichlorosilane)}.

[c] S1 = mol [(3-chloropropyl)trichlorosilane]/{mol [(3-chloropropyl)trichlorosilane] + mol (tetrachlorosilane)}.

[d] TOF = turnover frequency: mol allyl chloride converted per mol Pt and time.

[e] Wacker catalyst: mixture of dimeric Pt species with cyclooctadiene as ligand in such an amount to ensure a Pt concentration of about 500 ppm in a matrix of saturated hydrocarbons.

using relatively cheap and readily available $PtCl_4$ as the source of platinum. In contrast to the actual industrial system, no addition of extra ligands and no pre-formation of the Pt catalyst is required which simplifies the catalyst handling and reduces catalyst costs. This finding reflects the favourable solvation properties of the $[Tf_2N]^-$ ionic liquids for simple Pt salts such as $PtCl_4$.

Recycling Experiments in Repetitive Semi-Batch Mode

Once having ascertained that the ionic liquid biphasic concept can be successfully applied to the hydrosilylation of technically relevant chlorosilanes, we continued investigating the recyclability of the ionic catalyst solution. In such recycling experiments both the catalyst stability under reaction/separation conditions and the catalyst leaching behaviour are probed.

We chose [EMMIM] $[NTf_2]$ for these recycling experiments mainly due to the fact that this specific ionic liquid shows rapid (within less than ten seconds) phase separation from the reaction mixture. As a matter of fact, the time required for complete phase separation is of great relevance for dimensioning the settler unit with quicker phase separation allowing for a smaller separator unit in continuous operation.

In our recycling experiments, the ionic catalyst phase was allowed to separate from the product phase by gravity after each run, isolated under inert conditions and reused without further treatment, purification or activation. The results of the original run (Figure 1, run No. 0) and nine consecutive recycling experiments are presented in Figure 1 (not all the runs are depicted).

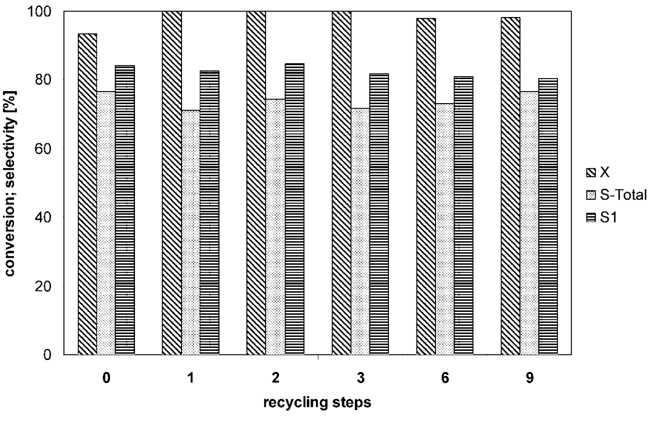


Figure 1. Pt-catalyzed liquid-liquid biphasic hydrosilylation of $HSiCl_3$ and allyl chloride – results of the recycling experiments in repetitive semi-batch mode (X = conversion %; S_{total} = mol [(3-chloropropyl)trichlorosilane]/{mol[(3-chloropropyl)trichlorosilane]} + mol(tetrachlorosilane) + mol (propyltrichlorosilane); S1 = mol [(3-chloropropyl)trichlorosilane]/{mol[(3-chloropropyl)trichlorosilane] + mol(tetrachlorosilane)]}.

As a result of these recycling experiments, no indication for a systematic loss in activity or selectivity was found. Remarkably, all recycling runs showed a higher selectivity compared to the monophasic experiments using the homogeneous "Wacker catalyst" (entry 4, Table 2). Given this excellent recyclability, we expected very low Pt leaching into the organic product phase. Indeed, this was confirmed by inductive coupled plasma-atom emission spectroscopy (ICP-AES) indicating that Pt leaching was below the detection limit of 1 ppm for all organic samples. In order to quantify a possible leaching of ionic liquid into the product phase, the collected organic phase samples of the nine recycling runs were united, concentrated by evaporation under high vacuum (150 °C, 10^{-3} mbar) to 5 mL of heavies and analyzed by ^1H NMR spectroscopy for the characteristic ionic liquid imidazolium peaks. Using this methodology, no hint for a leaching of the ionic liquid into the product phase could be obtained. The same concentrate was again analyzed by ICP-AES and also this residue showed no sign of Pt being present above the detection limit of our spectrometer.

Batch Autoclave Experiments

All hydrosilylation experiments described so far have been carried out in an open glass apparatus equipped with a very efficient condenser (cooling temperature: −10 °C; see Experimental Section). This cooling system was required to minimize evaporative losses of the trichlorosilane feedstock (bp = 31 °C). Obviously, this kind of open system operation is not very realistic to mimic a potential technical application of this biphasic ionic liquid-based hydrosilylation system. Therefore we decided to perform also a set of batch experiments in a closed autoclave reactor. This reactor was equipped with an overhead stirrer to provide optimum mixing conditions between the two liquid phases in the reactor. Moreover, a thermocouple was mounted to probe the temperature of the reaction mixture during reaction (for more details see Experimental Section). Table 3 presents the results of these experiments.

Unfortunately, we were not able to operate the autoclave isothermally when the organic phase consisted of pure feedstock at the start of the reaction. As can be seen from Table 3, entry 1, the strongly exothermic reaction in the autoclave led to an increase in temperature of more than 100 °C after 2 min reaction time. This behaviour could be ascribed to the limited cooling capacity of the applied autoclave equipment. To avoid such undefined thermal conditions we decided to reduce the concentration of feedstock in the reac-

Table 3. Hydrosilylation of allyl chloride and trichlorosilane in a batch autoclave reactor – test of different feedstock concentrations to ensure isothermal reaction conditions.[a]

Entry	Toluene added *vs.* reactants (molar ratio)	T_{max} (ΔT exotherm)	Conversion [%]	S_{total}[b] [%]	S1[c] [%]
1	None	200 °C (100 °C)	99.0	67.6	78.8
2	3:1	110 °C (10 °C)	94.7	72.3	80.3
3	5:1	< 103 °C (< 3 °C)	74.4.	76.2	81.4

[a] *Conditions:* 180 ppm $PtCl_4$ in [EMMIM] [Tf_2N], $HSiCl_3$/allyl chloride: 0.95:1.00, T_{start} = 100 °C, reaction time: 60 min, mass balance could be accounted for all experiments within 2%.

[b] S_{total} = mol [(3-chloropropyl)trichlorosilane]/{mol [(3-chloropropyl)trichlorosilane] + mol (tetrachlorosilane) + mol (propyltrichlorosilane)}.

[c] S1 = mol [(3-chloropropyl)trichlorosilane]/{mol [(3-chloropropyl)trichlorosilane] + mol (tetrachlorosilane)}.

tor by adding an inert solvent to the reaction mixture. Toluene was selected for this purpose as it can be easily dried and also forms a miscibility gap with the ionic liquid thus supporting rapid phase separation after the reaction.

Indeed, by using a diluted reactant phase the exotherm could be significantly reduced while reaching approximately isothermal conditions with a molar ratio of reactants/toluene of 1 to 5 (Table 3, entry 3). Under these conditions, the conversion was not complete after 60 min reaction time [X(silane) = 74.4%], as the reduced feedstock concentration resulted in a decrease of the reaction rate. From the comparison of entries 1–3 in Table 3, it can be seen that the exotherm in entries 1 and 2 led to the expected increase in reaction rate but to a reduced selectivity for the formation of (3-chloropropyl)trichlorosilane. Remarkably, the selectivities in the temperature-controlled, diluted system (Table 3, entry 3) were very similar to the undiluted, intensively cooled, atmospheric pressure system (comparison with entry 2, Table 2) proving that also in the autoclave experiment the ionic liquid biphasic approach can realize very attractive selectivities if proper heat removal and temperature control are realized.

Liquid-Liquid Biphasic Hydrosilylation in a Continuous Loop Reactor

Encouraged by these promising results we decided to transfer the concept of a biphasic hydrosilylation of chlorosilanes into a continuous reactor system. As stated above, the continuous flow operation mode permits a reliable and accurate "proof of concept". Especially, the long-term stability of the ionic catalyst solution can be more reliably probed under conditions that are close to the technical application scenario.

Realizing the continuous operation we aimed to immobilize the ionic catalyst solution over the whole reaction time in the reactor without any exchange or regeneration. At the same time, the biphasic exothermic character of the hydrosilylation reaction required intense mixing (to maximize the exchange surface) and a high ratio of heat exchange surface/reactor volume (for efficient heat removal). All these requirements were fulfilled in the best way by using a loop reactor as schematically shown in Figure 2. A similar reactor concept was formerly realized by our group and proven to be effective for the Ni-catalyzed dimerization of olefins using chloroaluminate ionic liquids.[17]

This rig can be compared to a mixer settler set-up with an internal phase recirculation. Due to a high volumetric flow in the recycle loop compared to the inflow of feed and the outflow of products, the reactor is fully back-mixed and shows the residence time distribution of a continuous stirred-tank reactor. The main reactor components are a static mixer (Figure 3, upper right side, providing a well defined fine dispersion) and a phase separator (Figure 3, left side) providing enough residence time for a full phase separation. During reaction, the liquid-liquid biphasic reaction mixture is circulated in the loop with high flow rates (up to 7 L/min). Under these conditions the

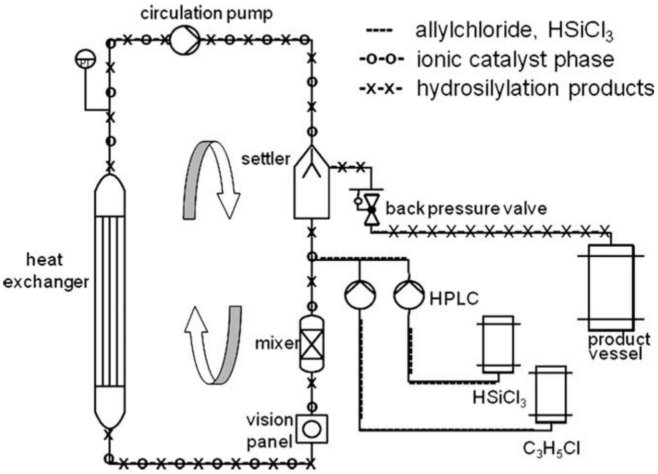


Figure 2. Scheme of the applied loop reactor for the biphasic Pt-catalyzed hydrosilylation of allyl chloride and trichlorosilane using [EMMIM] [Tf_2N] as catalyst immobilization phase.

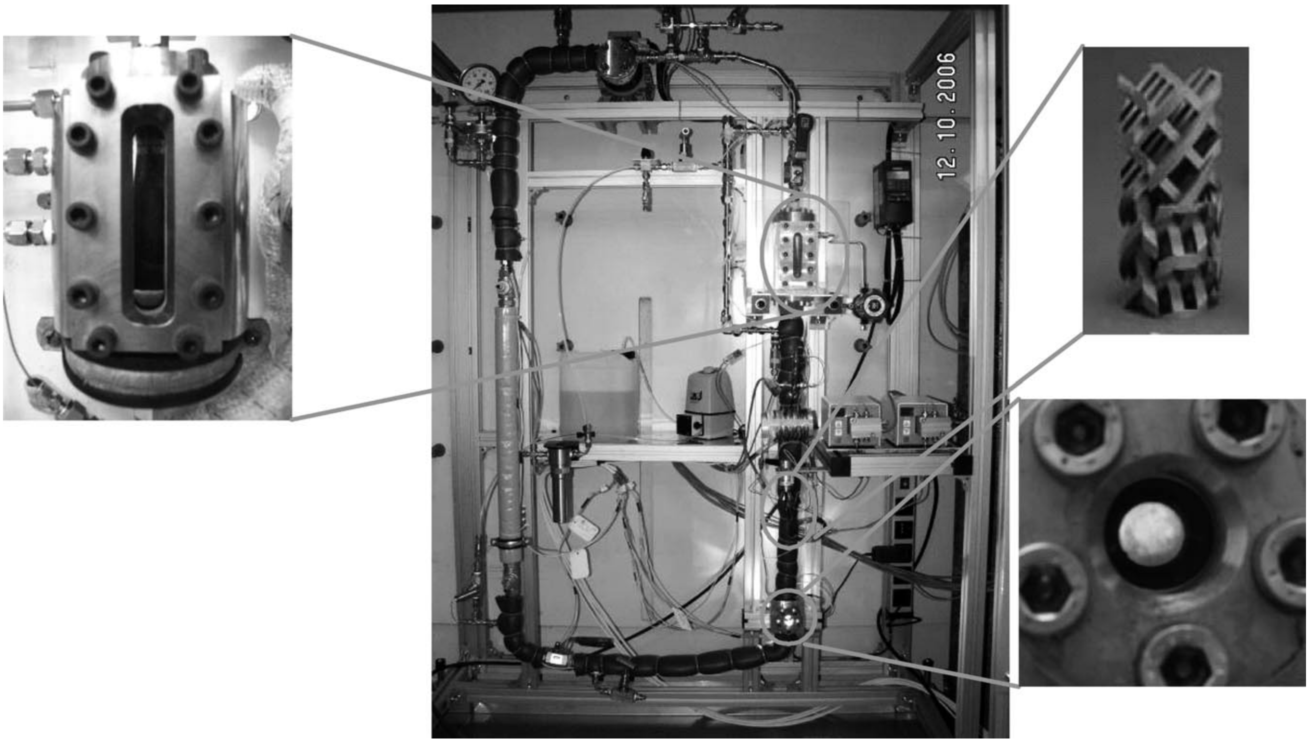


Figure 3. Detailed view of the continuous hydrosilylation loop reactor as applied.

static mixer (Sulzer ChemTech, TYP SMX DN10, 80 mm) – acting as micromixer elements in the reactor loop – provides an efficient dispersion of the ionic catalyst solution in the organic phase. The degree of dispersion can be monitored by an inspection window.

The droplet size of the ionic liquid and the exchange surface can be estimated using the following correlation.[18]

$$d_{\max} = (1+0.3\cdot\varepsilon_{mixer})\cdot\left(\frac{(1+1.3\cdot Vi)\cdot We_c}{2}\right)^{0.6}\cdot\left(\frac{\sigma}{\rho_{org.\,phase}}\right)^{0.6}\cdot\left(\frac{\rho_{org.\,phase}}{\rho_{IL}}\right)^{0.1}\cdot\varepsilon^{-0.4}$$

$$Vi = \left[\frac{\eta_{IL}\cdot(\varepsilon\cdot d_{\max})^{\frac{1}{3}}}{\sigma}\right]\cdot\sqrt{\frac{\rho_{org.phase}}{\rho_{IL}}}$$

where: ρ [kg/L] = density of organic and IL phase; ε [W/kg] = specific energy supply; σ [N/m] = surface tension; μ [Pas] = total viscosity; Vi [dimensionless] = viscosity number according to Calabrese;[19] and We_c [dimensionless] = critical Weber number.

The silane and the olefin feedstock were fed from two storage vessels with a maximum total inflow of 2.5 litres per hour. Two cooler/heater units ensured full temperature control in a temperature range up to 200 °C. The applied loop reactor had a volume of 650 mL and could be operated at pressures up to 100 bar. The main separation of the product from the ionic catalyst solution was realized in a gravity separator that was integrated in the reactor loop. In this way, most of the catalyst was always present in the reactor allowing for a direct investigation of the catalyst reactivity by analyzing the isolated products. Additionally, the system was also equipped with an external ionic liquid separator that was used to recycle small amounts of ionic liquid catalyst solution that left the reactor loop through the separator. This external separator unit was also used to collect ionic liquid samples for analytical purposes during reactor operation. 24 h/7 days operations were possible with the applied set-up due to a safety concept that monitored all critical parameters of the rig leading to an automatic safety shut-down if one critical parameter was out of range.

The following paragraphs describe the results of a typical hydrosilylation experiment in the continuous

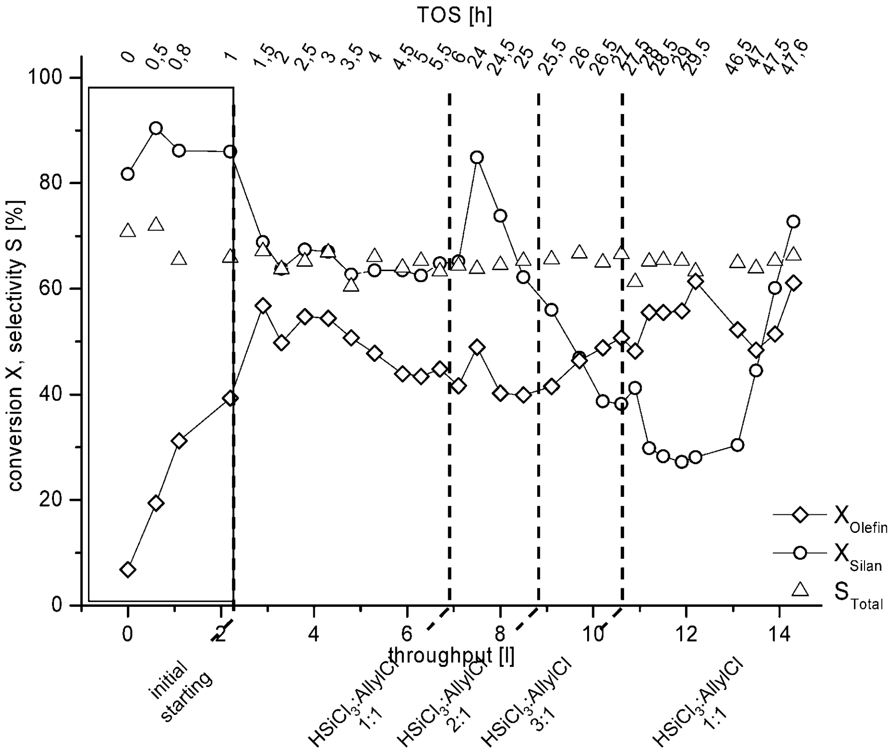


Figure 4. Results of a continuous hydrosilylation experiment in the loop reactor with varying silane/allyl chloride feed compositions (X = Conversion %).

loop reactor (details concerning the experimental procedure to run the rig are given in the Experimental Section). The results were obtained by applying an ionic catalyst solution of 150 g (100 mL) of [EMMIM] [Tf_2N] containing 400 ppm $PtCl_4$. This ionic catalyst solution was pumped into the loop reactor and the reactor filling was completed by addition of toluene up to complete flooding of the reactor. After that, the circulation pump was switched on and started the liquid-liquid biphasic mixing. With a volumetric flow of 3.2 $L\,min^{-1}$, the mean Sauter's diameter of the ionic-liquid dispersed droplets was estimated to be 0.27 mm (according to the above-mentioned correlation). To start the reaction, a mixture of trichlorosilane and allyl chloride was fed into the reactor. Figure 4 shows the conversion with respect to both feedstocks and the selectivities obtained for a run over 48 h time-on-stream (TOS) leading to a total organic throughput of more than 14 kg with an average conversion of more than 50%.

The reaction system needed 1.5 h time-on-stream (corresponding to 2.2 litres of organic throughput) to reach a first steady state. This finding corresponds with the well established empirical statement that the reactor volume of a loop reactor has to be exchanged three times (volume of loop reactor = 0.65 litre) to reach steady-state operation. This result clearly indicated a rapid *in situ* formation of the active Pt catalyst in the ionic liquid since the catalyst pre-formation step negligibly affected the time to reach steady-state operation.

The first steady-state conditions were kept for 4 h. During this time, approximately 4 litres of organic feedstock was transformed reaching conversions of 50–70% with respect to chlorosilane and allyl chloride. The fact that product analysis suggested different degrees of conversions for both feedstock molecules is explained by the fact that the by-product pathway to form tetrachlorosilane and trichloropropylsilane consumes two moles of silane, one to form the tetrachlorosilane and one to react with propene giving trichloropropylsilane.

In order to study the influence of the feedstock composition on the product selectivity, the silane/olefin ratio was varied in the subsequent hours of the experiment to roughly 2:1 (starting from 6.0 h TOS) and 3:1 (starting from 25.0 h TOS). Remarkably, no major changes in product selectivity were observed, only the specific conversions of chlorosilane and olefin changed according to the changing feedstock composition. The system in general proved to be very robust with respect to product selectivity, realizing total selectivities for (3-chlorpropyl)trichlorosilane in the range between 61% and 72% throughout the 48 h TOS.

For a proper interpretation of the data in Figure 4, it is important to mention that between TOS 6 h und 23 h as well as between 29.5 h and 45 h TOS the rig was continuously running overnight with greatly reduced feed throughput per hour in order to avoid overflow of tanks and sampling devices. Most interestingly, by re-adjusting the initial conditions of the first steady state after 48 h TOS (corresponding to a total organic throughput of 14.4 litres) it was possible to reach again the original conversion and selectivity values (comparison of steady state after 1.5 h TOS with conversion and selectivity after 48 h TOS). This finding proved impressively the operational stability of the ionic liquid-based biphasic system and the efficiency of the *in situ* catalyst separation and recycling.

Moreover, this remarkable operational stability provides also an impressive proof for the fact that Pt leaching into the organic phase was indeed far below 1 ppm (the detection limit of our ICP-AAS analysis) as can be shown by a simple calculation. In fact, over the 48 h TOS continuous operation, a constant Pt leaching of 1 ppm into the organic phase would have resulted in a total Pt leaching of 15 mg of Pt into the generated organic product. However, the total amount of $PtCl_4$ added to the ionic liquid was only 50 mg corresponding to a platinum mass of 29 mg. Thus, a 1 ppm Pt leaching should have caused roughly a loss of half the added Pt load with a consequent drop of activity which was clearly not observed. Moreover, by analyzing the Pt amount remaining in the ionic liquid after the 48 h TOS continuous operation, we could detect the same concentration of Pt as was initially added (within the error margin of our ICP-AAS analyses, typically ±5%). It is very remarkable that this excellent platinum immobilization was realized without the presence of any specific ligand or tailor-made ionic liquid structure.

Conclusions

In this paper, we have reported another successful application of biphasic transition metal catalysis, namely the Pt-catalyzed hydrosilylation reaction of allyl chloride with $HSiCl_3$ using bis(trifluoromethanesulfonyl)-imide salts as the catalyst immobilization phase. Our results impressively demonstrated the unique features ionic liquids can offer to homogeneous liquid-liquid biphasic catalysis. For this example, the combination of beneficial catalyst solvation, broad miscibility gaps and excellent chemical stability proved to result in a new and highly attractive approach to the Pt catalyzed hydrosilylation of trichlorosilane.

Compared to today's technically applied homogeneous Pt catalyst (the "Wacker catalyst"), the product selectivities in the studied biphasic ionic liquid systems proved to be 3–5% higher. Moreover, due to the solvation properties of the ionic liquid, the ionic liquid-based reaction can apply unmodified $PtCl_4$ as the Pt source. This fact avoids the need for specific ligands (that are required in the homogeneous system to provide enough Pt solubility) thus decreasing catalyst costs and simplifying catalyst handling.

After batch-mode screening experiments to identify the best ionic liquid and to optimize the reaction conditions, a continuous loop reactor with integrated ionic liquid separation and recycling was designed and tested. Using this reactor concept, operational stability of an ionic catalyst solution containing 400 ppm $PtCl_4$ has been achieved for 48 h. During the continuous experiment, stable conversions (50–70% with respect to both chlorosilane and olefin for different operating conditions) and very attractive, stable product selectivities [62–71% total selectivity to (3-chloropropyl)trichlorosilane] have been demonstrated. In agreement with this excellent operational stability, it was shown that Pt leaching into the organic product phase was far below 1 ppm of Pt without the need for any additional ligand to immobilize the metal in the ionic liquid phase.

We are convinced that the above-presented concept of biphasic ionic liquid organic hydrosilylation catalysis is of significant practical relevance and can be easily implemented even into already existing plants.

Experimental Section

General Remarks

Allyl chloride and trichlorosilane were obtained in technical grades from Wacker AG, Burghausen. [EMIM] [Tf_2N], [BMIM] [Tf_2N], [BMMIM] [Tf_2N], [OMA] [Tf_2N], [EMIM] [$EtSO_4$], [EMIM] [Et_2PO_4], [EMIM] [tosylate], [EMIM] [TfO], [BMIM] [PF_6] and [BMIM] [BF_4] were purchased from Solvent-Innovation GmbH, Cologne. All other ionic liquids were prepared from the chloride or bromide salts according to well known procedures.[20] All chemicals and precursors for the synthesis of the ionic liquids were obtained from commercial sources (Fluka, Aldrich, Merck) and used without further purification. All ionic liquids were dried for 6 h under high vacuum (10^{-3} mbar, 50 °C) to remove traces of water. The water content of all ionic liquids and allyl chloride was confirmed to be below 20 ppm by Karl–Fischer titration using a Metrohm 756 KF Coulometer with a Hydranal® Coulomat AG reagent. All experiments were carried out under strictly inert conditions using Schlenk-technique and argon as inert gas.

Preparation and Handling of the Ionic Catalyst Solution

$PtCl_4$ was added under an argon atmosphere to a pre-dried sample of ionic liquid in such an amount to give a 2000 ppm solution. The sample was stirred and complete solution was obtained after 20 min with all ionic liquids under investigation. Later, additional ionic liquid was added to obtain the desired catalyst concentration for the experiment. The baseline experiment with the "Wacker catalyst" was carried out by using a sample of the commercial homogeneous catalyst obtained from Wacker AG, Burghausen.

Experiments in a Semi-Batch Glass Reactor at Atmospheric Pressure

The hydrosilylation reactions under atmospheric conditions were carried out in a 150-mL three-necked-flask, immersed in an oil-bath with an automatic internal temperature controller. The flask was equipped with a dropping-funnel, a reflux condenser (cooling temperature $T_{cool}=-10\,°C$) and a magnetic stirrer. Prior to use, all glass-ware was dried under vacuum at 100 °C. 15 g of the ionic liquid catalyst solution prepared from the stock solution mentioned above were inserted directly into the tree-necked-flask. The reactants [12 g of trichlorosilane, 5.5 g of allyl chloride both dissolved in 5 g of the product trichloro(3-chloropropyl)silane for better heat control during the experiment] were introduced into the dropping funnel. The reaction was started *via* the addition of the reactants, whereby the dropping rate did not exceed the reflux rate. After the completion of the reaction, the content of the flask was collected with a 30-mL syringe and the organic layer allowed to separate from the ionic liquid.

Recycling Experiments in Repetitive Semi-Batch Mode

After the reaction, the ionic liquid was separated from the product phase by mean of a 30-mL syringe. The ionic liquid was reintroduced in the same glass reactor set-up mentioned above and reused without further treatment like distillation or extraction. Fresh feedstock was added *via* the dropping funnel.

Batch Experiments in Autoclave

The hydrosilylation reactions were carried out using an 80-mL stainless-steel autoclave with a 60-mL PTFE insert. The temperature was controlled both on the external surface and *via* an internal thermal element. The autoclave was equipped with a magnetic stirrer and a dropping funnel for setting a specific starting time. Prior to use the autoclave was dried under vacuum at 100 °C. All the chemicals were charged by using Schlenk techniques and under strictly inert conditions. The ionic liquid (2.5–7.5 mg $PtCl_4$ in 15 g [EMMIM] [BTA]) was inserted directly into the PTFE insert. The reactants (12 g of trichlorosilane and 5.5 g of allyl chloride) were introduced into the dropping funnel. The reaction was started *via* the addition of the reactants. For the concentration *vs.* time experiment samples were taken *via* a needle valve without loosing pressure. After the completion of the reaction, the reactor content was collected with a 30-mL syringe and the organic layer was separated from the ionic liquid.

For the recycling experiments the ionic liquid was reused without further treatment.

Continuous Experiments using a 650-mL Loop Reactor

150 g of ionic liquid with a total amount of $PtCl_4$ of 400 ppm were pumped into the loop reactor, which was dried under high vacuum for 12 h prior to the experiment. The feedstock of allyl chloride was delivered *via* an HPLC pump (0.4–40 $mL\,min^{-1}$). The equivalent amount of trichlorosilane was controlled *via* a rotameter and conveyed by using 15 bar of argon pressure. A back-pressure regulator ensured a constant excess pressure (0–60 bar). A circulation pump (0–8 $L\,min^{-1}$) guaranteed the residence time behaviour of a CSTR. At the gravimetric phase separator a diffuser slowed the velocity of the ionic liquid-product dispersion down, so that the ionic liquid settled and could be recirculated with the main amount of the organic phase. The amount of organic products discharged from the reactor corresponded exactly to the amount of feedstock added as the reactor was operated at all times in a fully flooded state. All non-gaseous products were collected in a 1000-mL Schlenk flask.

Product Analysis and Mass Balance

All GC analyses of the reaction mixtures were carried out using a Varian CP 3800 TCD with a 30 m Varian GS-Q column and helium as the mobile phase (carrier gas velocity $=1\,mL\,min^{-1}$). The silanes were detected using a WLD detector at a temperature of 300 °C. Due to low peak intensities, the samples were not quenched or diluted with additional solvents prior to analysis. The solvents were injected at 200 °C with a split of 0.01 using a temperature program from 110–250 °C. Correction factors for each reactant and product were determined and periodically confirmed. The mass balance was calculated from all components and could be accounted for all reported experiments within 2%.

ICP-AES Analysis

ICP-AES analyses were performed using a Spectro CirosCCP spectrometer at 1600 W at a wavelength of 214, 423 and 306, 471 nm. For sample preparation, 5 mL of organic or ionic liquid sample were quenched with 7 mL of ethanol in an ice-bath forming the related ethoxysilanes which are known to be more inert and easier to handle. These samples were then analyzed without further dilution by direct injection into the spectrometer. Prior to the measurements, the system was calibrated using a five-point standard regression with standard samples formed from 18 mL pure ionic liquid/25 mL ethanol/9 mL pure quenched ethoxysilanes for ionic liquid analysis and 25 mL ethanol/25 mL pure quenched ethoxysilanes for organic phase analysis. The platinum standard solution was purchased by Sigma Aldrich (Specpure 1000 $\mu g\,mL^{-1}$ in 20% HCl).

NMR Analysis

^1H and ^{19}F NMR spectra of the collected organic phase for traces of IL were recorded without further solvent using an insert tube filled with DMSO-d_6 on a Jeol ECX 400 spectrometer at 400 and 376 MHz, respectively.

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