J|A|C|S

ARTICLES

Published on Web 07/08/2006

Biphasic Hydrosilylation in Ionic Liquids: A Process Set for Industrial Implementation

Tilmann J. Geldbach,[†] Dongbin Zhao,[†] Nikola C. Castillo,[†] Gabor Laurenczy,[†]
Bernd Weyershausen,[‡] and Paul J. Dyson*,[†]

Contribution from the Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, and R&D Department, Oligomers/Silicones, Degussa AG, D-45127 Essen, Germany

Received February 21, 2006; E-mail: paul.dyson@epfl.ch

Abstract: The biphasic hydrosilylation of 1-hexadecene with siloxane B9800 in a range of ionic liquids is reported. Of the ionic liquids tested, [C_4py][BF_4] and [C_4-3-pic][BF_4] offer the optimum compromise between activity and catalyst retention. Several platinum precatalysts were screened, of which K_2PtCl_4 and Pt(PPh_3)$_4$ were found to give the best performance; the former provides the highest activity, while the latter offers higher stability and recyclability, and depending on the conditions, both can afford either homogeneous or soluble nanoparticle catalysts as the active species. A number of reaction parameters were varied, and the effects of oxygen, water, and chloride impurities on the reaction were studied. In addition, since nanoparticle catalysts were observed, various strategies to stabilize nanoparticles were screened, but none of them resulted in a superior catalytic system.

---

1. Introduction

Organomodified siloxanes account for approximately 15% of the entire silicone market[1] and are accessible in a number of ways, including variation of the siloxane chain length through an equilibration reaction, condensation of Si−Cl moieties with alcohols (affording Si−OR groups), or via the catalyzed hydrosilylation of Si−H functionalities with olefins. These approaches are summarized in Scheme 1.

The latter reaction, hydrosilylation, is particularly attractive as it is clean (e.g., no formation of HCl, unlike the condensation pathway) and highly efficient. For this transformation catalyst loadings of only a few ppm platinum (relative to the mass of the formed product) are often sufficient, and therefore attempts to recycle the catalyst are seldom made. One possibility of reclaiming the catalyst is by conducting the reaction using a "liquid−liquid" biphasic approach. The concept of biphasic catalysis has been around for several decades[2] and is currently applied on an industrial scale in, for example, hydroformylation[3] (Rhône-Poulenc Ruhrchemie Process) and olefin dimerization[4] (Shell Higher Olefin Process). More recently, ionic liquids have been recognized as potential media for the immobilization of catalysts and have been used with considerable success in a wide range of laboratory scale reactions.[5] Reports on biphasic hydrosilylation reactions are nevertheless scarce; notable examples include rhodium-catalyzed fluorous biphasic hydrosilylation of alkenes,[6] ketones, and enones[7] as well as the hydrosilylation of alkynes with rhodium complexes in an aqueous anionic micellar system, using sodium dodecyl sulfate as phase transfer agent.[8] Also, the platinum-catalyzed hydrosilylation of fatty acids has been reported in a multiphase thermomorphic solvent system (i.e., which upon heating reversibly forms a single phase).[9] With respect to employing ionic liquids as the catalyst immobilization phase, hydrosilylation has not yet been widely explored either, the published examples being summarized in Scheme 2. The reaction of terminal olefins with dimethylphenylsilane was reported using a perfluorated analogue of Wilkinson's catalyst.[10] Essential to the retention of this particular catalyst is the use of an imidazolium-based ionic liquid with a highly fluorinated anion, viz. [B{*p*-($SiMe_2$-$CH_2CH_2C_6F_{13}$)-C_6H_4}$_4$]$^-$, a viscous liquid at ambient temperature. With this system a total turnover number of 4000 after 15 cycles was achieved at ca. 4% loss of rhodium per cycle. In contrast, rhodium leaching with the same catalyst immobilized in a perfluorated molecular solvent was 3-fold higher. Platinum-catalyzed hydrosilylation of terminal alkynes has been performed in imidazolium and ammonium-based ionic liquids with H_2-

---

[†] Ecole Polytechnique Fédérale de Lausanne (EPFL).

[‡] Degussa AG.

(1) Stadtmüller, S. *Polymers & Polymer Composites* **2002**, *10*, 49.

(2) (a) Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 8716. (b) Joó, F.; Beck, M. T. *Magy. Kém. Folyóirat* **1973**, *79*, 189. (c) Manassen, J. In *Catalysis: Progress in Research*; Bassolo F., Burwell, R. L., Eds.; Plenum Press: London, 1973.

(3) (a) Kuntz, E. Fr. Pat. 2314910, 1975; (b) Cornils, B. *J. Mol. Catal. A: Chem.* **1999**, *143*, 1.

(4) Freitas, E. R.; Gum, C. R. *Chem. Eng. Prog.* **1979**, 73.

(5) (a) Geldbach, T. J.; Dyson, P. J. *Metal-Catalysed Reactions in Ionic Liquids*; Springer: 2005. (b) Yang Z.; Pan, W. *Enzyme Microb. Technol.* **2005**, *37*, 19. (c) Jain, N.; Kumar, A.; Chauhan S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (d) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459.

(6) de Wolf, E.; Speets, E. A.; Deelman, B.-J.; van Koten G. *Organometallics* **2001**, *20*, 3686.

(7) (a) Dinh, L. V.; Gladysz, J. A. *Tetrahedron Lett.* **1999**, *40*, 8995−8998. (b) Dinh, L. V.; Gladysz, J. A. *New J. Chem.* **2005**, *29*, 173.

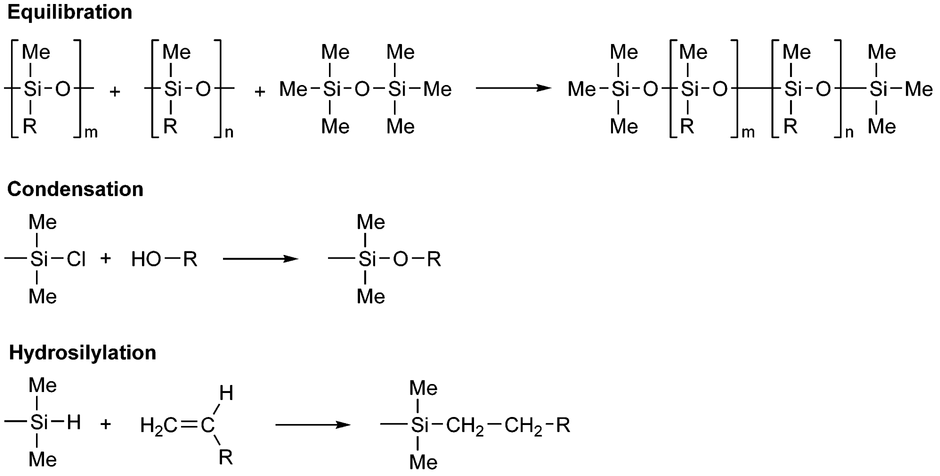
(8) Sato, A.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 2217.

(9) Behr, A.; Naendrup, F.; Obst, D. *Adv. Synth. Catal.* **2002**, *344*, 1142.

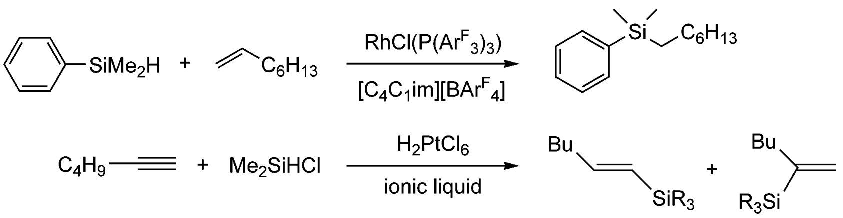
(10) van den Broeke, J.; Winter, F.; Deelman, B.-J.; van Koten, G. *Org. Lett.* **2002**, *4*, 3851.

10.1021/ja0612293 CCC: $33.50 © 2006 American Chemical Society

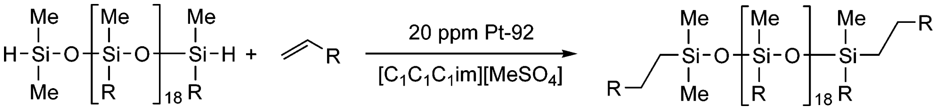
Scheme 1



Scheme 2



Scheme 3



$PtCl_6$ as catalyst with the products separated from the ionic liquid by distillation.[11]

Advantages of performing the reaction under biphasic conditions not only include the possibility of recycling the precious metal catalyst, but this methodology could also lead to a higher quality product. In homogeneous industrial hydrosilylation the platinum catalyst frequently remains in the product, resulting in tainted siloxanes, and catalyst immobilization in an ionic liquid offers the possibility of obtaining colorless products, which is particularly attractive if these materials are used as ingredients in cosmetics. Also, operating the reaction under biphasic conditions allows for better control of the exothermic reaction due to slower reaction kinetics.

In the literature of biphasic ionic liquid catalysis, the ionic liquid phase often contributes significantly to the total volume of the reaction mixture and sometimes even markedly exceeds the amount of employed substrate. However, for biphasic ionic liquid catalysis to be attractive from an industrial point of view, minimizing the amount of ionic liquid required is desirable, for reasons of cost and disposal (minimizing the amount of ionic liquid required also gives higher product yields per batch, i.e., volume/time-yield). In addition, it is essential that the catalyst is highly stable, catalyst immobilization is efficient, and ideally implementation into an already existing process should be simple, as should product isolation. Very promising results have been reported recently in the reaction between SiH-functionalized poly(dimethylsiloxane)s with terminal polyether olefins, using catalyst loadings as low as 20 ppm of platinum immobilized in approximately 1 vol % ionic liquid, illustrated in Scheme 3, fulfilling most of the above-mentioned requirements.[12] With certain catalyst/ionic liquid combinations, leaching of the catalyst into the product phase was below detection limits ($<$1 ppm) and catalyst recycling was possible several times without a marked decrease in activity, but commonly deteriorated after five to seven runs.

After these preliminary "proof-of-concept" studies we set out to study this reaction in more detail, attempting to ascertain the nature of the catalyst, with the ultimate aim of discovering a superior catalyst/ionic liquid system active and stable enough for industrial implementation. In this paper we describe the outcome from these experiments.

2. Results and Discussion

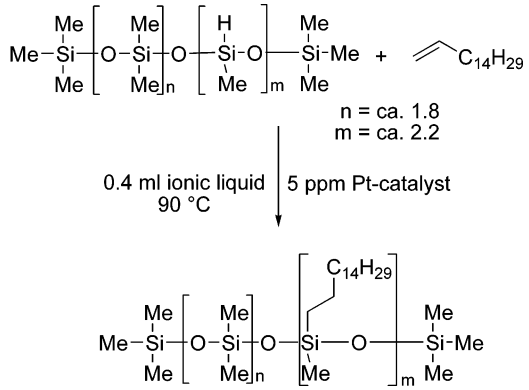
To make the biphasic ionic liquid hydrosilylation process suitable for implementation into Degussa's production facility, a target of at least 10 recycles was set, and thus, considerable improvements with respect to catalyst lifetime were required. From a combination of ^{195}Pt NMR spectroscopy and electrospray ionization mass spectrometry studies, it appeared that soluble nanoparticle catalysts might be involved.[13] With this in mind, the efficiency of biphasic (ionic liquid) hydrosilylation in the reaction between 1-hexadecene and a polydimethyl-methylhydrogen-polysiloxane (Siloxan B9800, Goldschmidt GmbH Ger-

---

(11) Aubin, S.; le Floch, F.; Carrié, D.; Guegan, J. P.; Vaultier, M. *ACS Symp. Ser.* **2002**, *818*, 334.

(12) (a) Weyershausen, B.; Hell, K.; Hesse, U. *ACS Symp. Ser.* **2005**, *902*, 133. (b) Weyershausen, B.; Hell, K.; Hesse, U. *Green Chem.* **2005**, *7*, 283. (c) Hell, K.; Hesse, U.; Weyershausen, B. Eur. Pat. Appl. EP1382630.

Scheme 4



many) (see Scheme 4) was studied at low catalyst concentrations, 5 ppm platinum (≈ 1.2×10^{-6} mol). Under such conditions catalyst stability and possible deactivation upon recycling and the influence of reaction parameters can be monitored more closely. It is noteworthy, however, that at these very low platinum loadings the catalyst is highly sensitive to the quality of the ionic liquid used and considerable effort has to be made to ensure that contaminants such as halides, water, and nonquarternarized ionic liquid cation precursors are absent (i.e., below the detection limit).

In the first instance, the nature of the catalyst phase was varied, testing liquids based on pyridinium, piccolinium, and imidazolium cations (see Figure 1) in combination with different anions, $[Tf_2N]^-$, $[BF_4]^-$, $[MeSO_4]^-$, $[SnCl_3]^-$, and $[N(CN)_2]^-$, with either K_2PtCl_4 or $Pt(PPh_3)_4$ as the platinum source. In preliminary experiments K_2PtCl_4 showed a comparable activity as H_2PtCl_6 (the so-called Speier's catalyst)[14] but offers the advantage of facilitated handling as the potassium salt is not hygroscopic. The catalyst phase was combined with the siloxane, 1-hexadecene was added dropwise at 90 °C within 15 min, and the progress of the reaction was monitored by measuring the amount of hydrogen gas formed upon reaction of an aliquot of the product phase with potassium butanolate (see Experimental Section).

The conversion after 3 h with respect to using the different ionic liquids and catalysts are summarized in Table 1, and the kinetic profiles of the reactions employing $[C_4\text{-4-pic}][BF_4]$ and $[C_4C_1\text{im}][BF_4]$ are shown in Figure 2 (kinetic data for the other ionic liquids are given in Table S1).

Catalyst immobilization is good in most cases in that the product phase remains colorless. Exceptions are the more lipophilic ionic liquids, namely $[C_2\text{-3-pic}][Tf_2N]$ and $[C_8\text{-3-pic}][BF_4]$, which result in a slightly yellow product phase due to leaching of the catalyst. Poor immobilization probably also explains why conversion is highest with these two ionic liquids, since mass transfer limitations will be minimized. Further, phase separation with such lipophilic liquids, be it either due to the presence of the $[Tf_2N]^-$ anion or a long alkyl chain, is slow, particularly as the product from the hydrosilylation reaction has a relatively high viscosity. Thus, it is also important that the reaction mixture is not stirred too vigorously; otherwise the ionic liquid is suspended into very small droplets which require a long time to separate from the product phase. A picture from a typical experiment is depicted in Figure 3, showing the magnetically stirred biphasic reaction mixture.

Both K_2PtCl_4 and $Pt(PPh_3)_4$ give very high initial turnover rates in most of the ionic liquids tested, despite the biphasic nature of the reaction (the conversion being slightly higher for K_2PtCl_4), and the reaction kinetic curves shown in Figure 2 for K_2PtCl_4 and $Pt(PPh_3)_4$ in $[C_4\text{-4-pic}][BF_4]$ and K_2PtCl_4 in $[C_4C_1\text{im}][BF_4]$ being indicative of homogeneously catalyzed reactions. Essentially no catalytic activity was observed with $[C_4C_1\text{im}][EtSO_4]$, $[C_4\text{-3-pic}][N(CN)_2]$, and $[C_4C_1\text{im}]Cl-SnCl_2$; $[C_4C_1\text{im}]Cl-SnCl_2$ was not stable under the reaction conditions, and the product phase became turbid. It is further interesting to note that, with both $[C_2C_1\text{im}][Tf_2N]$ and $[C_4C_1\text{im}][BF_4]$, a long induction period of more than 30 min is observed with $Pt(PPh_3)_4$ as the catalyst (see Figure 2 and Supporting Information), while high initial reaction rates are obtained with K_2PtCl_4. It has been demonstrated previously that $Pt^{(0)}(PR_3)_n$ complexes can react with 1,3-dialkylimidazolium salts to yield carbene complexes of the type $PtH(\text{carbene})(PR_3)_2$.[15] However, no hydride species could be detected in the ionic liquid after catalysis by means of ^1H NMR spectroscopy. Such sigmoidal kinetics curves are, however, indicative of nanoparticles catalysis in which the nanoparticles are generated in situ from a homogeneous precursor as the reaction proceeds.[16]

Further experiments employed the ionic liquids *N*-butyl-4-piccolinium tetrafluoroborate, $[C_4\text{-4-pic}][BF_4]$, and *N*-butylpyridinium tetrafluoroborate, $[C_4\text{py}][BF_4]$, as they combined both good conversion with good immobilization. A range of platinum precatalysts were tested with respect to their activity and stability in the latter solvent with results from these experiments listed in Table 2. In the course of our experiments it became clear that the quality of the ionic liquid is of key importance for the success of the reaction as different batches of ionic liquid led to significant variations in activity.

High activity was observed with all the platinum compounds tested. Nanoparticle formation occurs rapidly with $PtCl_2(\text{cod})$, $[PtCl_2(C_6H_{10})]_2$, and K_2PtCl_4 precatalysts (see below), and agglomerates of platinum black are visible in the ionic liquid phase. To increase the conversion, the reactions were also conducted at higher temperature, increasing to 110 °C after complete addition of the olefin. While higher reaction rates and higher conversions are achieved, the catalyst lifetime and recyclability are reduced, with an increase in the amount of platinum black precipitate observed under these more forcing conditions, following repeated recycling from all of the platinum sources. Figure 4 shows TEM images of nanoparticles with an approximate diameter of 3−4 nm originating from $PtCl_2(PPh_3)_2$ after five catalytic runs and also shows that some agglomeration of the nanoparticles has taken place.

In addition to platinum, the samples subjected to TEM analysis showed high concentrations of silicon (determined by

---

(13) Dyson, P. J.; McIndoe, J. S.; Zhao, D. *Chem. Commun*. **2003**, 508. In this paper we show that ESI-MS can be used to analyze molecular catalysts at very low concentrations directly in ionic liquids. However, while the catalyst precursor dissolved in the ionic liquid could be detected, no platinum species were observed after catalysis. Similarly, conducting the reaction in situ in an NMR tube resulted in loss of the platinum ^{195}Pt signal during the course of the reaction.

(14) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191.

(15) (a) McGuinness, D. S.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 8317. (b) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671 and references therein.

(16) (a) Weddle, K. S.; Aitken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653. (b) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A* **2003**, *191*, 187.

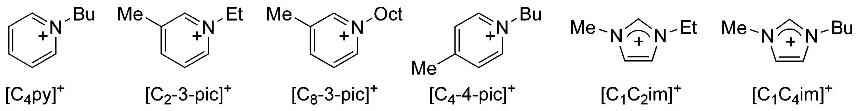


Figure 1. Ionic liquid cations used.

Table 1. Conversion after 180 min at 90 °C in Different Ionic Liquids

	K_2PtCl_4	$Pt(PPh_3)_4$
[C_2-3-pic][Tf_2N]	99%	97%
[C_2-3-pic][$MeSO_4$]	93%	86%
[C_4-3-pic][$N(CN)_2$]	<5%	<5%
[C_4py][BF_4]	98%	92%
[C_4-4-pic][BF_4]	97%	91%
[C_8-3-pic][BF_4]	99%	94%
[C_2C_1im][$EtSO_4$]	<5%	<5%
[C_2C_1im][Tf_2N]	94%	85%
[C_4C_1im][BF_4]	92%	75%
[C_4C_1im]Cl-$SnCl_2$	<5%	<5%

Table 2. Effect of Platinum Source on Catalytic Activity; 5 ppm Catalyst in 0.4 mL of [C_4py][BF_4], 60 min at 90 °C

	cycle 1	leaching[a]	cycle 2	IL color
$PtCl_2$(cod)	99%	yes	84%	brown + black precipitate
$PtCl_2(PPh_3)_2$	85%	no	85%	faint yellow suspension
$Pt(PPh_3)_4$	89%	no	89%	faint yellow
$[PtCl_2(C_6H_{10})]_2$	92%	slight	93%	brown + black precipitate
K_2PtCl_4	94%	no	93%	light brown + black precipitate

[a] Visible leaching, i.e., coloration of the product phase.

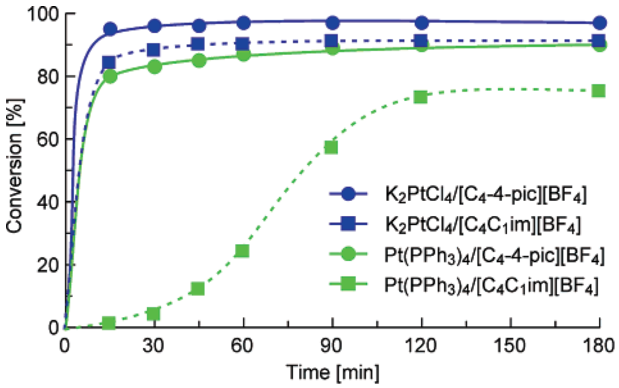


Figure 2. Reaction kinetics with 5 ppm catalyst immobilized in [C_4-4-pic][BF_4] (●) and [C_4C_1im][BF_4] (■) at 90 °C.

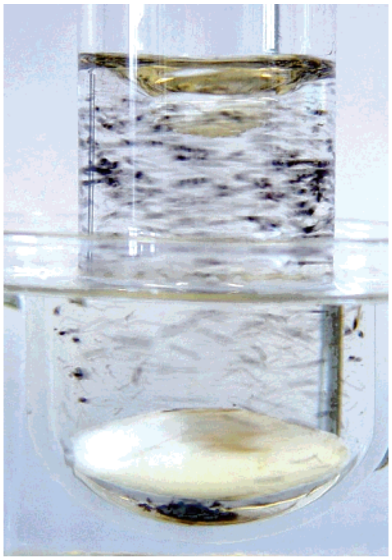


Figure 3. Biphasic hydrosilylation reaction with <1 vol % [C_4-4-pic][BF_4] as catalyst phase, containing a preformed nanoparticle catalyst.

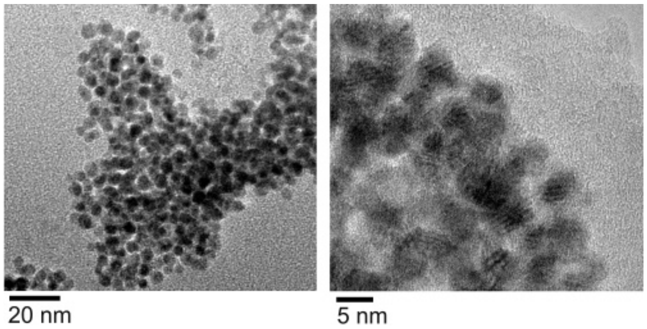


Figure 4. Platinum nanoparticles (3−4 nm diameter) isolated from $PtCl_2(PPh_3)_2$ after five catalytic cycles at 110 °C in [C_4-4-pic][BF_4].

EDX analysis), and Figure 5 shows nanoparticles and their corresponding elemental composition isolated after 10 cycles at 90 °C with $PtCl_2(PPh_3)_2$ as the catalyst precursor and [C_4-py][BF_4] as the immobilization phase.

In some instances, large amorphous areas were also observed in the TEM samples that did not contain any platinum but consisted mainly of silicon and oxygen. Most likely, these are derived from trace impurities present in the siloxane (or byproducts formed in the course of the reaction) that accumulate in the ionic liquid. In some cases the physical properties of the [C_4-4-pic][BF_4] ionic liquid altered during the course of recycling, generally resulting in an increase in viscosity. In TEM pictures from other hydrosilylation experiments the isolated particles from the ionic liquid were blurred and appeared to be coated by another substance, possibly rendering the nanoparticles inaccessible in further reactions. Such contamination of the ionic liquid may thus account for some of the observed decrease in catalytic activity during recycling experiments. However, maintaining the reaction temperature below 100 °C, and filtering the siloxane through a micropore filter (0.2 μm) prior to use, minimized these effects, and recycling was improved.

Catalyst stability upon repeated recycling was investigated with K_2PtCl_4, $[PtCl_2(C_6H_{10})]_2$, $PtCl_2(PPh_3)_2$, and $Pt(PPh_3)_4$ precatalysts in [C_4py][BF_4] at a catalyst loading of 5 ppm, and the conversions are shown in Figure 6. In addition, K_2PtCl_4 and $Pt(PPh_3)_4$ were also evaluated in [C_4-4-pic][BF_4], and data from these experiments are compiled in Table 3 and compared to those from the reaction with [C_4py][BF_4]. As it has become evident from the reaction kinetics (vide supra) that prolonged reaction times do not lead to a marked increase in product conversion, recycling studies were performed with reaction times of 1 h in order to maximize the lifetime of the catalyst.

While the initial activity with K_2PtCl_4 and $[PtCl_2(C_6H_{10})]_2$ is highest, these precatalysts also show the largest decrease in conversion upon repeated recycling, the latter becoming almost completely inactive after the eighth cycle. Conversion remains relatively stable for the other three precatalysts for at least 10

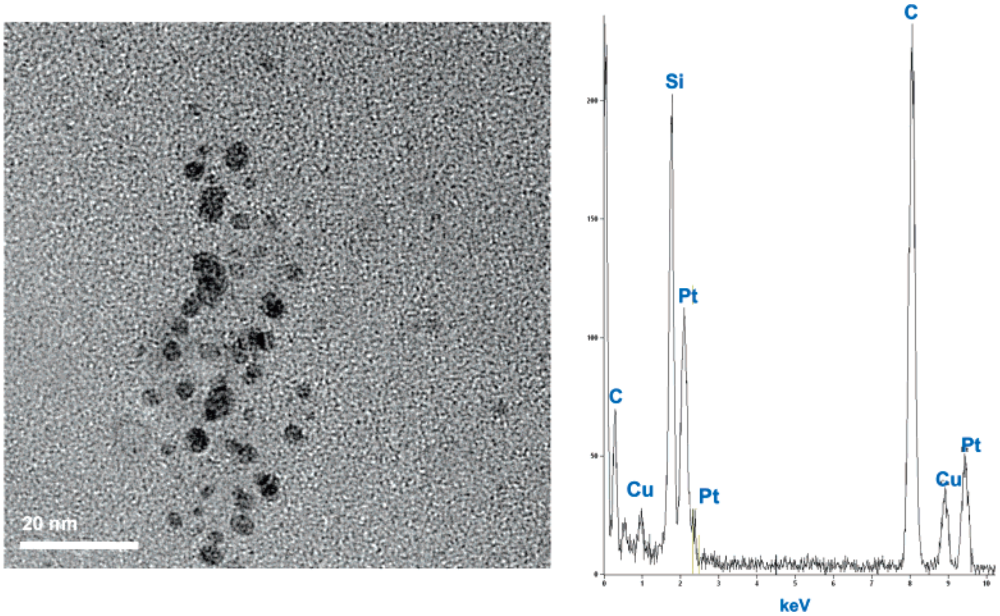


Figure 5. Platinum nanoparticles (2−4 nm diameter) isolated from $PtCl_2(PPh_3)_2$ after 10 catalytic cycles at 90 °C in $[C_4py][BF_4]$: (left) TEM images and (right) EDX spectrum.

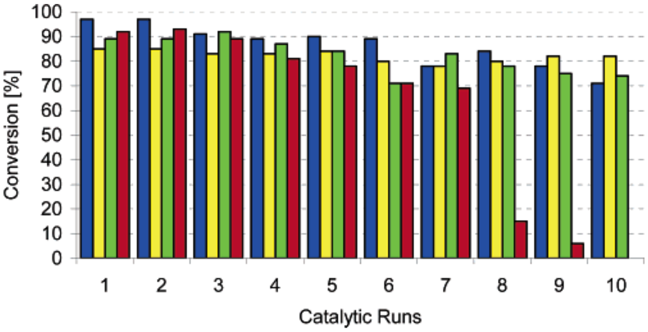


Figure 6. Catalyst recycling under inert (N_2) conditions with K_2PtCl_4 (blue), $[PtCl_2(C_6H_{10})]_2$ (red), $PtCl_2(PPh_3)_2$ (yellow), and $Pt(PPh_3)_4$ (green) in $[C_4py][BF_4]$; 5 ppm catalyst, 90 °C, 60 min/run.

Table 3. Catalyst Recycling under Inert (N_2) Conditions with K_2PtCl_4 and $Pt(PPh_3)_4$ in $[C_4py][BF_4]$ and $[C_4\text{-4-pic}][BF_4]$, 5 ppm Catalyst in 0.4 mL of Ionic Liquid, 60 min at 90 °C

	K_2PtCl_4 $[C_4\text{-4-pic}][BF_4]$ 5 ppm	K_2PtCl_4 $[C_4py][BF_4]$ 5 ppm	$Pt(PPh_3)_4$ $[C_4\text{-4-pic}][BF_4]$ 5 ppm	$Pt(PPh_3)_4$ $[C_4py][BF_4]$ 5 ppm	$Pt(PPh_3)_4$ $[C_4py][BF_4]$ 15 ppm
run 1	88%	97%	80%	89%	88%
run 2	92%	97%	81%	89%	93%
run 3	90%	91%	78%	92%	91%
run 4	80%	89%	77%	87%	88%
run 5	<5%	90%	76%	84%	86%
run 6		89%	64%	71%	81%
run 7		78%	72%	83%	88%
run 8		84%	73%	78%	88%
run 9		78%	33%	75%	87%
run 10		71%	<5%	74%	84%

runs with an average conversion of >86% with K_2PtCl_4 and >82% with $PtCl_2(PPh_3)_2$, corresponding to turnover numbers exceeding 1 500 000. After 10 catalytic cycles all the ionic liquids are pale yellow in color, irrespective of the precatalyst employed, and some platinum black is visible with the K_2PtCl_4 and $[PtCl_2(C_6H_{10})]_2$ catalyst precursors.

When the amount of $Pt(PPh_3)_4$ catalyst was increased from 5 to 15 ppm, no marked increase in activity was observed, indicating that already with 5 ppm catalyst mass transfer is limiting the reaction kinetics, and this observation is in good agreement with previous results.[12] Higher catalyst loadings are, however, beneficial with respect to the recyclability of the ionic liquid/catalyst solution in that, for example, the average conversion after 10 cycles using $Pt(PPh_3)_4$ in $[C_4py][BF_4]$ increased from 82% with 5 ppm to 87% with 15 ppm catalyst.

In general, higher conversions are obtained in $[C_4py][BF_4]$ compared to $[C_4\text{-4-pic}][BF_4]$; see Table 3 (graphs are shown in the Supporting Information). In addition, using K_2PtCl_4 as the catalyst precursor, the activity decreases more rapidly with recycling in comparison to $Pt(PPh_3)_4$, which shows excellent stability for eight runs. It is worth noting that, in the case of $[C_4\text{-4-pic}][BF_4]/Pt(PPh_3)_4$, the catalyst mixture was stored for 2 weeks at ambient temperature under nitrogen after the fifth run, showing that while storage is possible, it is not ideal. The solution from $[C_4\text{-4-pic}][BF_4]$ and $Pt(PPh_3)_4$ turned orange-red upon repeated recycling, and it is believed that trace amounts of organic impurities in the ionic liquid are responsible for this phenomenon. Such contaminants probably also explain the differences in activity and recyclability between $[C_4py][BF_4]$ and $[C_4\text{-4-pic}][BF_4]$, and again, it appears that uttermost care has to be taken with respect to the purification of the employed ionic liquids.

The presence of oxygen has been noted to facilitate certain platinum catalyzed hydroformylation reactions; it has been proposed that oxygen may help disrupt multinuclear (inactive) platinum species.[17] Accordingly, the effect of an oxygen atmosphere on catalyst performance and stability with either K_2PtCl_4 and $Pt(PPh_3)_4$ was investigated, demonstrating that the presence of oxygen leads to a marked decrease in activity, particularly for the precatalyst K_2PtCl_4; see Supporting Information. Despite the lower activity, the recyclability is not impaired under aerobic conditions, and if anything, it is slightly improved. There is also a visible difference in the ionic liquid phase in the presence of oxygen, as the ionic liquid solution containing K_2PtCl_4 in the course of recycling becomes deep red in color

---

(17) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

Table 4. Catalyst Recycling in the Presence of Mercury; 5 ppm Catalyst in 0.4 mL of [C_4-4-pic][BF_4], 60 min at 90 °C

	K_2PtCl_4	$Pt(PPh_3)_4$
run 1	85%	84%
run 2	32%	84%
run 3	7%	73%

without the formation of platinum black, while under inert atmosphere the solution turns light brown and contains a black precipitate. These observations indicate that the presence of oxygen indeed suppresses the formation of larger platinum agglomerates.

The significance of nanoparticle formation was further evaluated by conducting the hydrosilylation reaction with K_2PtCl_4 and $Pt(PPh_3)_4$ in the presence of a few drops of elemental mercury as a selective poison for nanoparticles (see Table 4). Activity decreases rapidly with K_2PtCl_4 after the first run, indicating that nanoparticles, either as catalyst reservoirs or as active catalysts in their own right, play a significant role in the catalysis, although not only in the absence of homogeneous catalysis. The relatively high conversion in the first run further points toward two different catalytically active species, with a homogeneous catalyst dominating in the early stages of the reaction and heterogeneous (soluble nanoparticle) catalysis dominating as the turnover numbers increase for K_2PtCl_4. A much smaller effect is observed with $Pt(PPh_3)_4$, which displays a comparable activity as in the absence of mercury for the first two cycles, with a slight decrease in the third run. It is quite conceivable that in the course of catalyst recycling the nature of the catalyst for all the precursors changes from a molecular to soluble nanoparticle species. Indeed, some platinum particles could also be isolated from $Pt(PPh_3)_4$/[C_4-4-pic][BF_4] solutions after several catalytic runs, however at lower concentration compared to when K_2PtCl_4 is used as the platinum source.

Common contaminants in ionic liquids include halides (chloride) and water, and they strongly influence the physical properties of the ionic liquid[18] and catalyzed reactions that take place in them.[19] The influence on the activity and recyclability of $Pt(PPh_3)_4$ was investigated, comparing the results from pure $Pt(PPh_3)_4$/[C_4-4-pic][BF_4] solutions with those containing either 5 mg/mL Cl or 50 μL/mL H_2O and a mixture of both. Addition of chloride leads to a color change from yellow to red, suggesting that a new complex is formed. Nevertheless, the chloride impurity resulted in only a minor deterioration in the first and second cycle. A more pronounced effect was observed with the wet ionic liquid. In the first run, a slightly higher conversion, 85% versus 81%, was observed, which might be due to lower viscosity of the wet ionic liquid, but conversion then decreased to 71% in the second run. Deterioration of activity was most pronounced when both water and chloride were present, affording rather poor catalytic activity of 67% and 53% in the first and second cycle, respectively, clearly demonstrating the necessity to employ pure ionic liquids for optimum results.

The nature of the active catalyst in platinum-catalyzed hydrosilylation remains a matter of much debate and depends on the reaction conditions, substrates and catalyst precursor employed.[20,21] A mononuclear homogeneous platinum complex has been proposed to be the active catalyst in the Chalk−Harrod mechanism,[22] which is believed to take place in, for example, the hydrosilylation of olefins with a mixture of $PtCl_2$ and PPh_3.[23] There are also strong indications that the hydrosilylation reaction is often catalyzed by Pt-nanoparticles. An in situ determination of the active catalyst was recently undertaken, combining features from both the Chalk−Harrod as well as the nanoparticle pathway.[20] Platinum on carbon has been demonstrated to be a catalyst for the hydrosilylation of alkenes and alkynes as early as 1953,[24] and similar selectivities and rates have been observed with Pt/C relative to Karstedt's catalyst.[25] We also found that Pt/C, when suspended in [C_4-4-pic][BF_4], did indeed catalyze the reaction between 1-hexadecene and siloxane, but it is also known that platinum can leach from the carbon support in C−C coupling reactions, thereby not providing absolute proof for the activity of nanoparticles. However, it appears that in many instances platinum nanoparticles are formed in the course of the hydrosilylation reaction by the presence of SiH functionalities, especially when electronegative substituents are present on the silane.[26] General indications for nanoparticle formation in platinum catalyzed hydrosilylation reactions include the presence of an induction period prior to the reaction and a characteristic yellow color of the product containing the catalyst (more extensive tests for nanoparticles catalysis have been described for other types of reactions).[27] Furthermore, platinum nanoparticles have been isolated after catalysis in a number of cases and analyzed by TEM.[25,26,28]

While there is no doubt that nanoparticles are formed in the course of hydroformylation reactions (such reactions have even been applied for the deliberate synthesis of platinum colloids),[29] the nature of the catalytically active species appears to depend on a number of factors. Nevertheless, the use of nanoparticles preformed under well-defined conditions may be advantageous, and accordingly, several different types of preformed nanoparticles catalysts were investigated. Ionic liquids have, in several instances, been shown to stabilize nanoparticles,[30] and nanoparticles prepared in ionic liquids, e.g., by reduction of a metal complex with molecular hydrogen, exhibit high activity and stability in, for example, the hydrogenation of arenes.[31] It has also been shown that well-dispersed palladium nanoparticles form in situ in nitrile-functionalized ionic liquids in certain C−C

---

(18) Seddon, K. R.; Stark, A.; Torres, M.-J. *Pure Appl. Chem.* **2000**, *72*, 2275.

(19) (a) Chauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed.* **1995**, *34*, 2698. (b) Gallo, V.; Mastrorilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P. *J. Chem. Soc., Dalton Trans.* **2002**, 4339. (c) Klingshirn, M. A.; Broker, G. A.; Holbrey, J. D.; Shaughnessy, K. H.; Rogers, R. D. *Chem. Commun.* **2002**, 1394. (d) Dyson, P. J. *Transition Met. Chem.* **2002**, *27*(4), 353. (e) Daguenet, C.; Dyson, P. J. *Organometallics* **2004**, *23*, 6080.

(20) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693 and references therein.

(21) Jagadeesh, M. N.; Thiel, W.; Köhler, J.; Fehn, A. *Organometallics* **2002**, *21*, 2076.

(22) Chalk, A. J.; Harrod, J. F. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 673.

(23) Skoda-Földes, R.; Kollár, L.; Heil, B. *J. Organomet. Chem.* **1989**, *366*, 275.

(24) (a) Wagner, G. H.; Stroher, C. O. U.S. Patent 2632013, 1953. (b) Wagner, G. H. U.S. Patent 2637738, 1953.

(25) Chauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645*, 1.

(26) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693 and references therein.

(27) For example, see: Dyson, P. J. *Dalton Trans.* **2003**, 2964 and references therein.

(28) Huang, J.; He, C.; Liu, X.; Xiao, Y.; Mya, K. Y.; Chai, J. *Langmuir* **2004**, *20*, 5145.

(29) Huang, J.; Liu, Z.; Liu, X.; He, C.; Chow, S. Y.; Pan, J. *Langmuir* **2005**, *21*, 699.

(30) (a) Umpierre, A. P.; Machado, G.; Fecher, G. H.; Morais, J.; Dupont, J. *Adv. Synth. Catal.* **2005**, *347*, 1404. (b) Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Texeira, S. R. *Inorg. Chem.* **2003**, *42*, 4738.

(31) (a) Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Texeira, S. R.; Dupont, J. *Chem.—Eur. J.* **2003**, *9*, 3263. (b) Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Texeira, S. R. *Inorg. Chem.* **2003**, *42*, 4738.

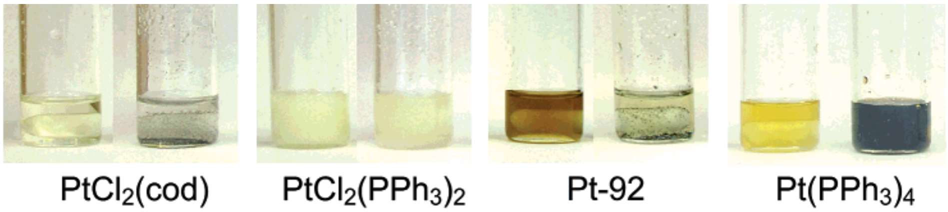
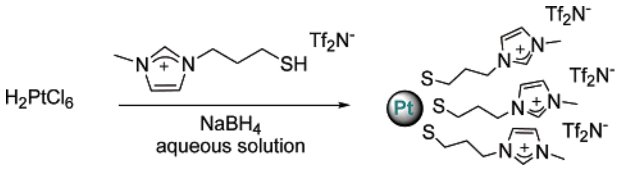


Figure 7. Platinum complexes in [C_4-4-pic][BF_4] before and after treatment with hydrogen gas (40 bar, 80 °C, 1 h).

Scheme 5



coupling reactions.[32] However, use of ionic liquids containing a nitrile functionality in the hydrosilylation reaction led to a marked decrease in activity, and addition of small amounts of a nitrile-functionalized ionic liquid (2.5−10%) to [C_4-4-pic]-[BF_4] did not lead to any improved recyclability. In an attempt to generate platinum nanoparticles prior to catalysis, ionic liquid solutions containing different platinum sources were pressurized with hydrogen gas at elevated temperatures. Pictures of these solutions before and after pressurization are shown in Figure 7. Both $PtCl_2$(cod) and [$PtCl_2(C_6H_{10})]_2$ give a deposit of platinum black, and these mixtures result in only poor substrate conversion (less than 20% conversion after 3 h). With these complexes formation of metallic platinum occurs very rapidly resulting in large aggregates which presumably offer only a small active surface. Following the hydrogen pretreatment the solution containing $Pt(PPh_3)_4$ becomes dark brown, while there is no visual change with $PtCl_2(PPh_3)_2$. In both cases there is no marked change in activity of the ionic liquid/catalyst phase relative to those that were not pretreated with hydrogen gas.

Platinum nanoparticles were also synthesized by reduction of H_2PtCl_6 with $NaBH_4$ in the presence of a thiol-functionalized ionic liquid according to a literature method;[33] see Scheme 5. The nanoparticles obtained in this way were redispersed in [C_4-4-pic][BF_4] and evaluated in the hydrosilylation reaction. A conversion of 94% was obtained only after 5 h, and the catalyst remained relatively stable for four runs but decreased markedly in activity in the fifth run (<50% conversion).

The approach described above was extended to using an ionic polymer as support:[34] an imidazolium derivative containing a styrene functionality was prepared and then polymerized to afford an imidazolium-tagged polystyrene (ILP) (see Scheme 6). An aqueous solution of H_2PtCl_6 was then reduced with $NaBH_4$ and then transferred to [C_2-3-pic][Tf_2N] with the assistance of Li[Tf_2N], and the resulting polymer-stabilized nanoparticles dispersed in [C_2-3-pic][Tf_2N] were tested in the hydrosilylation reaction.

A conversion of 88% was obtained within 60 min, but activity decreased to 25% in the second run. It was found that under reaction conditions the particles agglomerated and settled at the interface of the ionic liquid and product phase, as shown in Figure 8.

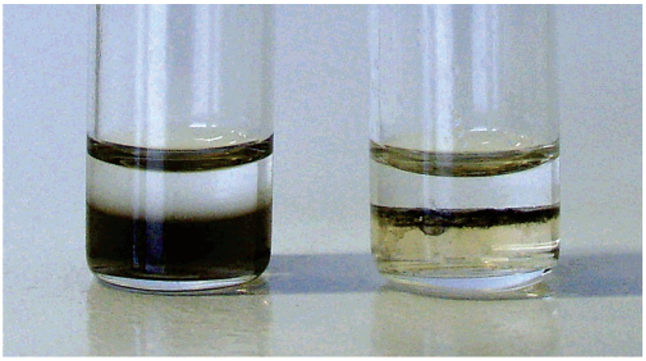
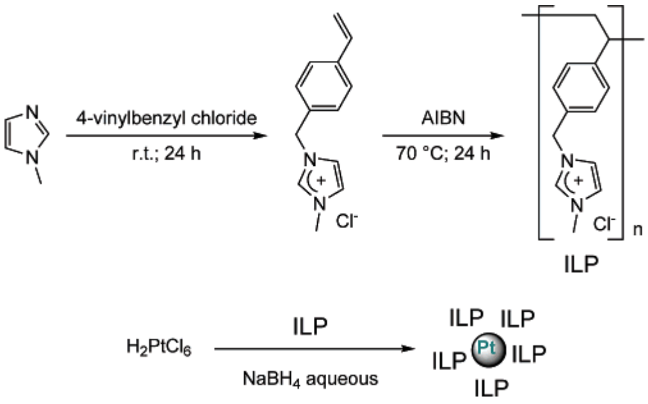


Figure 8. Polymer-stabilized nanoparticles in [C_2-3-pic][Tf_2N] before (left) and after (right) hydrosilylation.

Scheme 6



From these experiments it is clear that the in situ generated nanoparticles, combined with some degree of homogeneous catalytic activity, are most effective for the hydrosilylation reaction. This conclusion is in fact the ideal situation as the ionic liquid system can therefore easily be implemented into the current industrial process.

Concluding Remarks

Biphasic ionic liquid hydrosilylation is a highly attractive process, and catalyst recycling is possible for up to 10 cycles with only a small decrease in activity, depending on the reaction conditions and the employed catalyst and ionic liquid. The product can be simply isolated following precipitation of the catalyst-ionic liquid phase, which can be reused without any further treatment. While the catalytic activity was found to be markedly higher with simple platinum salts such as K_2PtCl_4 or complexes containing very labile ligands such as [$PtCl_2$-$(C_6H_{10})]_2$, a somewhat higher catalyst stability was observed with the molecular precatalysts $PtCl_2(PPh_3)_2$ and $Pt(PPh_3)_4$,

---

(32) (a) Zhao, D.; Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 15876. (b) Chiappe, C.; Pieraccini, D.; Zhao, D.; Fei, Z.; Dyson, P. J. *Adv. Synth. Catal.* **2006**, *348*, 68.

(33) Kim, K.-S.; Demberelnyamba, D.; Lee, H. *Langmuir* **2004**, *20*, 556.

(34) (a) Mu, X.-D.; Meng, J.-Q.; Li, Z.-C.; Kou, Y. *J. Am. Chem. Soc.* **2005**, *127*, 9694. (b) Zhao, D.; Fei, Z.; And, W. H.; Dyson, P. *Small* **2006**, *2*, 879.

despite these complexes not being charged![35] The active species in the catalysis could not be identified unambiguously under the chosen conditions, and it is possible that several different active species, i.e., nanoparticle as well as molecular catalysts, operate at the same time. In the case of nanoparticles, one possible mode of deactivation is by accumulation of (solid) impurities in the ionic liquids, which appear to coat the particles, rendering them inaccessible to the substrates. The targets set by Degussa were met, and it is anticipated that the ionic liquid process will be transferred from the pilot plant to industrial scale soon.

Experimental Section

1-Hexadecene (Acros technical grade) was distilled from sodium, siloxane B9800 (Goldschmidt) degassed, and passed through a 0.2 μm pore filter prior to use. The ionic liquids [C_8-3-pic][BF_4] and [C_4-3-pic][$N(CN)_2$] were a gift from Lonza; [C_2C_1im][$EtSO_4$] was obtained from Solvent Innovation; and [C_2-3-pic][Tf_2N], [C_2-3-pic][$MeSO_4$], [C_2-3-pic][Tf_2N],[36] [C_4-4-pic][BF_4],[37] [C_4C_1im][BF_4],[38] [C_4C_1im][Tf_2N],[39] [C_4C_1im]Cl−$SnCl_2$,[40] and [HSC_3C_1im][Tf_2N][41] were prepared according to methods reported in the literature. All other substances were purchased from Aldrich and were used as received.

Synthesis of Thiol-Stabilized Pt-Particles. A freshly prepared solution of $NaBH_4$ (2.0 mg, 0.054 mmol) in water (2 mL) was added dropwise to a mixture of H_2PtCl_6·6 H_2O (5.0 mg) and [$HS(CH_2)_3$im]-[Tf_2N] (0.25 mL) in water (10 mL). The resulting hydrophobic solid was separated by centrifugation and washed with ethanol (3 × 5 mL) to afford the imidazolium-stabilized nanoparticles.

Synthesis of Polymer-Stabilized Pt-Particles. To an aqueous solution of H_2PtCl_6 (2 mL, 6×10^{-4} mol/L), an aqueous solution of ILP (2 mL, 0.25 wt %) was added. The mixture was vigorously agitated, and $NaBH_4$ in water (2 mg in 1 mL) was added dropwise. The solution rapidly changes from yellow to dark brown. The aqueous solution of Pt-nanoparticles was mixed with [C_2-3-pic][Tf_2N] (2 mL), and Li[Tf_2N] (100 mg) was added. After dynamic shaking, the Pt-nanoparticles were transferred into the [C_2-3-pic][Tf_2N] phase.

Catalytic Hydrosilylation. In a typical experiment, degassed siloxane B9800 (22 mL, 0.047 mol) was heated to 90 °C, and ionic liquid (0.4 mL) containing ca. 1.16×10^{-6} mol Pt-catalyst (= 5 ppm Pt relative to the total mass of substrates) was added. Then, 1-hexadecene (32 mL, 0.111 mol) was added under a stream of nitrogen dropwise within ca. 15 min, and stirring continued at 90 °C for another 45 min under inert conditions. At the end of the reaction the two phases were allowed to separate, the product was decanted or removed with a syringe, and the ionic liquid solution recharged with fresh siloxane for the next catalytic run. Conversion of the reaction was established by measuring the amount of hydrogen gas liberated upon reaction of the product with 3% potassium butanolate in 1-butanol according to the following formula:

$$100 - \frac{Volume\ H_2\ gas\ [mL] \cdot 0.004}{Sample\ weight\ [g] \cdot 0.2239} = Conversion[\%]$$

Catalytic Hydrosilylation under Aerobic Conditions: As above, however, prior to the addition, the siloxane was saturated with oxygen gas and the reaction was carried out under a gentle stream of oxygen.

TEM Sample Preparation and TEM Analysis. Method 1: The ionic liquid containing nanoparticles were diluted with dichloromethane, and the nanoparticles were separated by centrifugation. The separated nanoparticle powders were redispersed in methanol. Specimens for TEM were prepared by depositing a drop of this nanoparticle dispersion on a carbon-coated copper grid (400 mesh). The copper grid was then dried at ambient temperature.

Method 2: The ionic liquid containing nanoparticles (0.5 mL) was diluted with dichloromethane (10 mL), and then a drop was deposited onto a copper grid directly. The copper grid was then dried under a vacuum before insertion into the microscope.

A PHILIPS CM20 transmission electron microscope was used, and the EDX data were collected on a Thermo Noran System Six X-ray microanalysis system combined with the CM20 TEM.

Acknowledgment. Financial support by Degussa and the Swiss National Science Foundation is gratefully acknowledged.

Supporting Information Available: Kinetic data with different ionic liquids, additional graphs, and pictures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0612293

---

(35) Dyson, P. J. *Appl. Organomet. Chem.* **2002**, *16*, 495.

(36) (a) Nekrasov, L. N.; Almualla, H.; Khomchenko, T. N.; Smirnov, Yu. D.; Tomilov, A. P. *Elektrokhimiya* **1994**, *30*, 75. (b) Waserscheid, P.; Metlen, A.; Brausch, N. PCT Int. Appl. 2005, WO 2005014547 A1 20050217 CAN 142:221616 AN 2005:141032.

(37) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. *J. Chem. Eng. Data* **2001**, *46*, 1526.

(38) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; De Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217.

(39) Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Graetzel, M. *Inorg. Chem.* **1996**, *35*, 1168.

(40) Valkenberg, M. H.; deCastro, C.; Holderich, W. F. *Appl. Catal., A* **2001**, *215*, 185.

(41) Baleizao, C.; Gigante, B.; Garcia, H.; Corma, A. *Tetrahedron Lett.* **2003**, *44*, 6813.