

# Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/ionic liquid (molten salt) as a thermoregulated and recyclable catalytic system for hydrosilylation

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## Abstract

We have investigated the use of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/ionic liquid (molten salt) as a thermoregulated and recyclable catalytic system for hydrosilylation. It was found that both conversion and selectivity could be influenced by the alkyl chains attached to the pyridinium and imidazolium cations. The Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/ionic liquid (molten salt) catalyst system combines the advantages of an ionic liquid with convenient product separation, whilst the catalyst system can be reused at least 10 times without noticeable decrease of activity and selectivity.

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**Keywords:** Hydrosilylation; *N,N*-Dialkylimidazolium hexafluorophosphate; *N*-Alkylpyridinium hexafluorophosphate; Recyclable

## 1. Introduction

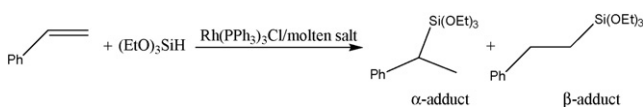
Hydrosilylation is one of the most important Si–C bond formation reactions in organosilicon chemistry. Many organosilicon monomers containing functional groups have been synthesized via this reaction [1]. Though the catalytic hydrosilylation process is well established, and platinum, rhodium or other transition metal-based catalysts are widely used, it is still desirable to further increase catalytic activity and selectivity and to minimize the amount of catalyst. Recently, ionic liquids have been considered as environmentally benign media for catalytic processes; much attention has been focused on organic reactions that employ ionic liquids as solvents for the homogeneous transition metal catalyst, in which the catalyst is dissolved and immobilized [2–7]. Currently, the advantages of biphasic catalysis including organic solvent/ionic liquid, supercritical carbon dioxide/ionic liquid and supported ionic liquid

catalysis have attracted much attention [8–11]. van den Broeke et al. [12] reported a novel fluoros room-temperature ionic liquid, 1-butyl-3-methyl-imidazolium tetrakis[*p*-{dimethyl-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]-borate, which was used as a solvent for the hydrosilylation of 1-octene catalyzed by a fluoros version of Wilkinson's catalyst. The catalyst was recycled by biphasic separation with an average retention of catalyst activity of 94%. However, the preparation of this ionic liquid was difficult and expensive. Very recently, Weyershausen et al. [13] reported a platinum catalyzed hydrosilylation process in an ionic liquid, and for which the catalyst/ionic liquid system was recyclable.

Inspired by the research work of van den Broeke et al. [12] and Weyershausen et al. [13] on hydrosilylation reactions in ionic liquid media, together with interest in the characteristics of the ionic liquid itself, we have designed a new hydrosilylation process in which *N*-alkylpyridinium hexafluorophosphate salts or *N,N*-dialkylimidazolium hexafluorophosphate organic molten salts were used as the support for Wilkinson's catalyst. The reactions were conducted in a liquid–liquid biphasic system followed by separation from a liquid–solid biphasic system. The hydrosilylation of different olefins with triethoxysilane was carried out to evaluate the effect

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Scheme 1. Hydrosilylation of styrene with triethoxysilane catalyzed with  $\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{molten salt}$ .

of different alkyl substituents attached to cations on the catalytic activity and selectivity of  $\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{molten salts}$  (Scheme 1).

## 2. Experimental

### 2.1. General methods

Tetrahydrofuran (THF) was distilled from benzophenone over sodium wire. Styrene was washed with 5% NaOH and dried with  $\text{Na}_2\text{SO}_4$ . After filtration the styrene was distilled under reduced pressure. All other substances were purchased from Aldrich and were used as received.  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  was prepared according to a procedure from the literature [14].

The GC–MS: Trace DSQ GC–MS Column: DB-5 30 m  $\times$  2.5 mm  $\times$  0.25  $\mu\text{m}$ ; split: 50:1; flow: 1 ml/min const flow; inlet temp: 260  $^\circ\text{C}$ ; column temp: 50  $^\circ\text{C}$  (hold 1 min) then 15  $^\circ\text{C}/\text{min}$  up to 260  $^\circ\text{C}$  (hold 10 min).

### 2.2. Synthesis of 1-benzylimidazole

1-Benzylimidazole was synthesized by selective Hoffmann-type elimination of the 2-cyanoethyl group from the imidazolium salt obtained by the reaction of benzyl bromide with 1-(cyanoethyl)imidazole [15,16]. A mixture of imidazole (8.2 g, 0.12 mol), acrylonitrile (15 mL, 0.225 mol) and methanol (15 mL) were added to a 100 mL round-bottomed flask equipped with a stirrer and reflux condenser. After the mixture was stirred for 16 h under reflux, the excess acrylonitrile and solvent were removed by rotary evaporation under reduced pressure to yield a yellow liquid 1-(cyanoethyl)imidazole, which was used without further purification. Benzyl bromide (17.1 g, 0.1 mol) and acetonitrile (15 mL) were mixed with the 1-(cyanoethyl)imidazole. The mixture was stirred at 85  $^\circ\text{C}$  for 10 h and then evaporated to dryness. The residue was mixed with 15% aqueous NaOH (30 mL), stirred for 1 h, and then ethyl ether (50 mL) was added. The organic phase was separated from the aqueous phase and washed with brine to remove any water-soluble impurities. The organic phase was dried with  $\text{MgSO}_4$  and evaporated; a white solid (14.3 g, 91% overall yield) was obtained. An analytical sample was prepared by recrystallization from ethyl ether: white crystal, mp 69.7–69.8  $^\circ\text{C}$ ; MS (EI)  $m/z$  (%): 159 ( $[\text{M} + \text{H}]^+$ , 12), 158 ( $\text{M}^+$ , 72), 91 (100);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  5.12 (s, 2H,  $\text{CH}_2$ ), 6.90–7.36 (m, 8H, PhH, ImH).

### 2.3. Synthesis of organic molten salts

All the organic molten salts *N*-ethylpyridinium hexafluorophosphate ( $\text{EtPyPF}_6$ ), *N*-butylpyridinium hexafluorophosphate ( $\text{BuPyPF}_6$ ), *N*-hexylpyridinium hexafluorophosphate ( $\text{HexPyPF}_6$ ), *N*-octylpyridinium hexafluorophosphate ( $\text{OctPyPF}_6$ ), *N*-hexadecylpyridinium hexafluorophosphate ( $\text{C}_{16}\text{PyPF}_6$ ), *N*-

benzylpyridinium hexafluorophosphate ( $\text{BnPyPF}_6$ ), 1-benzyl-3-methylimidazolium hexafluorophosphate ( $\text{BnMeImPF}_6$ ), 1-benzyl-3-ethylimidazolium hexafluorophosphate ( $\text{BnEtImPF}_6$ ), 1-benzyl-3-butylimidazolium hexafluorophosphate ( $\text{BnBuImPF}_6$ ), 1-benzyl-3-hexylimidazolium hexafluorophosphate ( $\text{BnHexImPF}_6$ ), 1-benzyl-3-octylimidazolium hexafluorophosphate ( $\text{BnOctImPF}_6$ ) and 1,3-dibenzylimidazolium hexafluorophosphate ( $\text{Bn}_2\text{ImPF}_6$ ) were prepared according to literature procedures [17,18]. All the prepared compounds showed spectroscopic data ( $^1\text{H NMR}$ ) in accordance with the assigned structure.

*N*-Ethylpyridinium hexafluorophosphate ( $\text{EtPyPF}_6$ ) mp 103.2–103.4  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$ : 1.02 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 4.67 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 8.11–8.98 (m, 5H, PyH).

*N*-Butylpyridinium hexafluorophosphate ( $\text{BuPyPF}_6$ ) mp 71.3–73.2  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.82 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.21–1.90 (m, 4H,  $-\text{CH}_2$ ), 4.47 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 7.93–8.64 (m, 5H, PyH).

*N*-Hexylpyridinium hexafluorophosphate ( $\text{HexPyPF}_6$ ) mp 42.1–42.8  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.87 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.25–2.00 (m, 8H,  $-\text{CH}_2$ ), 4.58 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 7.99–8.69 (m, 5H, PyH).

*N*-Octylpyridinium hexafluorophosphate ( $\text{OctPyPF}_6$ ) mp 65.4–65.5  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.84 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.23–2.00 (m, 12H,  $-\text{CH}_2$ ), 4.55 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 8.00–8.71 (m, 5H, PyH).

*N*-Hexadecylpyridinium hexafluorophosphate ( $\text{C}_{16}\text{PyPF}_6$ ) mp 117.6–119.1  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.86 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.24–1.98 (m, 28H,  $-\text{CH}_2$ ), 4.58 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 8.03–8.73 (m, 5H, PyH).

*N*-Benzylpyridinium hexafluorophosphate ( $\text{BnPyPF}_6$ ) mp 103.2–103.4  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$ : 5.83 (s, 2H,  $\text{CH}_2$ ), 7.45–7.52 (m, 5H, PhH), 8.10–9.08 (m, 5H, PyH).

1-Benzyl-3-methylimidazolium hexafluorophosphate ( $\text{BnMeImPF}_6$ ) mp 130.6–131.7  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 3.99 (s, 3H,  $\text{NCH}_2$ ), 5.34 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 7.11–7.45 (m, 7H, PhH, ImH), 8.59 (s, 1H, ImH).

1-Benzyl-3-ethylimidazolium hexafluorophosphate ( $\text{BnEtImPF}_6$ ) mp 82.1–83.0  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.54 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 4.22 (q,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 5.30 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 7.21–7.35 (m, 7H, PhH, ImH), 8.60 (s, 1H, ImH).

1-Benzyl-3-butylimidazolium hexafluorophosphate ( $\text{BnBuImPF}_6$ )  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.84 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.25–1.82 (m, 4H,  $\text{CH}_2$ ), 4.10 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 5.29 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 7.20–7.42 (m, 7H, PhH, ImH), 8.73 (s, 1H, ImH).

1-Benzyl-3-hexylimidazolium hexafluorophosphate ( $\text{BnHexImPF}_6$ )  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.82 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.25–1.89 (m, 8H,  $\text{CH}_2$ ), 4.10 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 5.26 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 7.21–7.35 (m, 7H, PhH, ImH), 8.62 (s, 1H, ImH).

1-Benzyl-3-octylimidazolium hexafluorophosphate ( $\text{BnOctImPF}_6$ ) mp 90.8–92.5  $^\circ\text{C}$ ,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.85 (t,  $J = 8$  Hz, 3H,  $\text{CH}_3$ ), 1.22–1.83 (m, 12H,  $\text{CH}_2$ ), 4.12 (t,  $J = 8$  Hz, 2H,  $\text{NCH}_2$ ), 5.29 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 7.19–7.37 (m, 7H, PhH, ImH), 8.77 (s, 1H, ImH).

Table 1

Effect of organic molten salts on the hydrosilylation reaction of styrene and triethoxysilane catalyzed with Rh(PPh<sub>3</sub>)<sub>3</sub>Cl

Entry	Catalyst <sup>a</sup>	Conv. (%)	Selectivity (%)			
			β	α	1-Ethylbenzene	β/α
1 <sup>b</sup>	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	49.3	62.2	27.0	10.8	2.3
2 <sup>b</sup>	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/Dichloromethane	70.7	69.3	21.2	9.5	3.3
3 <sup>b</sup>	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/THF	62.3	72.6	17.1	10.3	4.2
4	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	100	90.6	5.3	4.1	17.1
5	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BuPyPF <sub>6</sub>	98.6	88.7	4.1	7.2	21.6
6	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/HexPyPF <sub>6</sub>	95.4	87.4	3.4	9.2	25.7
7	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/OctPyPF <sub>6</sub>	92.3	86.5	3.1	10.4	27.9
8	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/C <sub>16</sub> PyPF <sub>6</sub>	91.5	85.2	2.7	12.1	31.6
9	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnPyPF <sub>6</sub>	92.8	93.9	1.8	4.3	52.2
10	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnMeImPF <sub>6</sub>	93.2	93.1	1.7	5.2	54.8
11	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnEtImPF <sub>6</sub>	93.0	93.6	1.2	5.2	78.0
12	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnBuImPF <sub>6</sub>	92.8	94.1	0.8	5.1	117.6
13	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnHexImPF <sub>6</sub>	92.4	94.6	0.5	4.9	189.2
14	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnOctImPF <sub>6</sub>	91.9	95.3	0.1	4.6	953.0
15	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/Bn <sub>2</sub> ImPF <sub>6</sub>	91.1	95.7	–	4.3	

Reaction conditions: styrene 2.5 mmol; triethoxysilane 3.0 mmol; 90 °C, 5 h.

<sup>a</sup> Catalyst Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/*N*-alkylpyridinium hexafluorophosphate or *N,N*-dialkylimidazolium hexafluorophosphate 0.4 g, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 0.1 mol% based on styrene.<sup>b</sup> Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 2.0 mg.

1,3-Dibenzylimidazolium hexafluorophosphate (Bn<sub>2</sub>ImPF<sub>6</sub>) mp 124.9–125.8 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 5.31 (s, 4H, CH<sub>2</sub>Ph), 7.06–7.41 (m, 12H, PhH, ImH), 8.89 (s, 1H, ImH).

#### 2.4. Preparation of organic molten salts supported catalyst

The typical procedure for preparation of organic molten salts supported catalyst was as follows: 0.4 g of the required organic molten salt (EtPyPF<sub>6</sub>, BuPyPF<sub>6</sub>, HexPyPF<sub>6</sub>, OctPyPF<sub>6</sub>, C<sub>16</sub>PyPF<sub>6</sub>, BnPyPF<sub>6</sub>, BnMeImPF<sub>6</sub>, BnEtImPF<sub>6</sub>, BnBuImPF<sub>6</sub>, BnHexImPF<sub>6</sub>, BnOctImPF<sub>6</sub> or Bn<sub>2</sub>ImPF<sub>6</sub>) was mixed with 2.0 mg of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl. The mixture was heated to about 100–120 °C and stirred for 2 h under nitrogen. After cooling to room temperature the solid was ground up and used as a catalyst for the hydrosilylation of alkylene with triethoxysilane.

#### 2.5. Hydrosilylation of alkylene with triethoxysilane

Typical hydrosilylation reaction procedures were as follows: a given amount of catalyst was introduced into a 10 mL round-bottomed flask equipped with magnetic stirring, then the alkene and silane were added. This mixture was heated to the appropriate temperature, and the hydrosilylation reaction was allowed

to proceed with constant stirring for 5 h. At the end of the reaction, the product phase was separated from the catalyst by decantation, and the conversion of alkene and the selectivity were determined by GC–MS. The catalyst was recharged with fresh alkene and silane for the next catalytic run.

### 3. Results and discussion

#### 3.1. Effect of different organic molten salts on the hydrosilylation reaction

For the hydrosilylation reactions carried out in organic solvents such as THF and dichloromethane as well as under solvent-free conditions, Wilkinson's catalyst Rh(PPh<sub>3</sub>)<sub>3</sub>Cl had low catalytic activity and selectivity (Table 1, entries 1–3). However, when the complex Rh(PPh<sub>3</sub>)<sub>3</sub>Cl was mixed with an organic molten salt, it exhibited greater catalytic activity and selectivity. It was also found that the catalytic activities of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/*N*-alkylpyridinium hexafluorophosphate and *N,N*-dialkylimidazolium hexafluorophosphate decrease slightly with increasing length of the alkyl chain. In contrast, the ratio of the β-adduct to α-adduct (β/α), clearly, increases; in particular, no α-adduct could be detected at all when Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/Bn<sub>2</sub>ImPF<sub>6</sub>

Table 2

Effect of the amounts of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl on the hydrosilylation reaction of styrene with triethoxysilane

Entry	Catalyst	Conv. (%)	Selectivity (%)			β/α
			β	α	1-Ethylbenzene	
1	1%Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	100	90.7	5.3	4.0	17.1
2	0.5%Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	100	90.6	5.3	4.1	17.1
3	0.25%Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	98.6	90.1	5.1	4.8	17.7
4	0.15%Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	92.4	90.3	5.0	4.7	18.1
5	0.1%Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	81.9	89.9	5.0	5.1	18.0
6	0.05%Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	61.6	88.7	5.1	6.2	17.4

Reaction conditions: styrene 2.5 mmol; triethoxysilane 3.0 mmol; 90 °C, 5 h; catalyst Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/EtPyPF<sub>6</sub> 0.4 g.

Table 3  
Effect of temperature on the hydrosilylation reaction of styrene with triethoxysilane

Entry	Catalyst	T (°C)	Conv. (%)	Selectivity (%)			$\beta/\alpha$
				$\beta$ -Product	$\alpha$ -Product	1-Ethylbenzene	
1	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	70	98.8	90.6	5.2	4.2	17.4
2		90	100	90.6	5.3	4.1	17.1
3		110	100	90.1	5.3	4.6	17.0
4	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnPyPF <sub>6</sub>	90	92.8	93.9	1.8	4.3	52.2
5		110	96.3	92.9	2.0	5.1	46.5
6		130	99.2	91.7	2.0	6.3	45.9
7		150	100	90.1	2.2	7.7	41.0
8	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnMeImPF <sub>6</sub>	90	93.2	93.1	1.6	5.3	58.2
9		100	95.4	92.8	1.6	5.6	58.0
10		120	98.9	92.9	1.7	5.4	54.6
11		130	100	93.2	1.8	5.0	51.8

Reaction conditions: styrene 2.5 mmol; triethoxysilane 3.0 mmol; 5 h; catalyst Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/*N*-alkylpyridinium hexafluorophosphate or *N,N*-dialkylimidazolium hexafluorophosphate 0.4 g.

was used as the catalyst (Table 1, entry 15). This result indicates that the substituents attached to the organic molten salt cation have a strong impact on the catalytic process.

### 3.2. Effect of the amount of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl and reaction temperature on the hydrosilylation reaction

The hydrosilylation reactions were examined in the presence of 1.0 mol%, 0.5 mol%, 0.25 mol%, 0.15 mol%, 0.1 mol% and 0.05 mol% of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl, respectively. The conversions of styrene were 100, 100, 98.6, 92.4, 81.9, 61.6%, respectively, and the selectivities of the  $\beta$ -product were 90.7, 90.6, 90.1, 90.3, 89.9, 88.7%, respectively (Table 2). Although the conversion of

styrene increased with increasing amounts of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl used, the selectivities were constant.

The effects of temperature are illustrated in Table 3. This shows that the conversion of styrene increases with increasing reaction temperature. However, the ratio  $\beta/\alpha$  decreased slightly with increase of reaction temperature.

### 3.3. Hydrosilylation of other aliphatic alkenes

When aliphatic alkenes such as 1-hexene, 1-heptene, 1-octene and 1-undecene replace styrene as one of the substrates, excellent conversions and selectivities are obtained with different Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/molten salts (Table 4).

Table 4  
Results of the hydrosilylation reaction of aliphatic alkenes with triethoxysilane

Entry	Alkylene	Catalyst	Conv. (%)	Selectivity (%)		
				$\beta$	$\alpha$	Alkane, etc.
1	1-Hexene	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	100	99.8	–	0.2
2		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BuPyPF <sub>6</sub>	100	99.7	–	0.3
3		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/HexPyPF <sub>6</sub>	100	99.8	–	0.2
4		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/OctPyPF <sub>6</sub>	100	99.9	–	0.1
5		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/C <sub>16</sub> PyPF <sub>6</sub>	100	99.5	–	0.5
6		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnPyPF <sub>6</sub>	100	99.6	–	0.4
7		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnMeImPF <sub>6</sub>	100	99.6	–	0.4
8		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnEtImPF <sub>6</sub>	100	99.5	–	0.5
9		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnBulImPF <sub>6</sub>	100	99.6	–	0.4
10		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnHexImPF <sub>6</sub>	100	99.4	–	0.6
11		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnOctImPF <sub>6</sub>	100	99.7	–	0.3
12		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/Bn <sub>2</sub> ImPF <sub>6</sub>	100	99.3	–	0.7
13	1-Heptene	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	100	99.6	–	0.4
14		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnOctImPF <sub>6</sub>	100	99.2	–	0.8
15	1-Octene	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	~100	99.7	–	0.3
16		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnOctImPF <sub>6</sub>	~100	99.4	–	0.6
17	1-Undecene	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/EtPyPF <sub>6</sub>	~100	99.8	–	0.2
18		Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl/BnOctImPF <sub>6</sub>	~100	99.5	–	0.5

Reaction conditions: alkylene 2.5 mmol; triethoxysilane 3.0 mmol; Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/*N*-alkylpyridinium hexafluorophosphate or *N,N*-dialkylimidazolium hexafluorophosphate 0.4 g; 90 °C, 5 h.

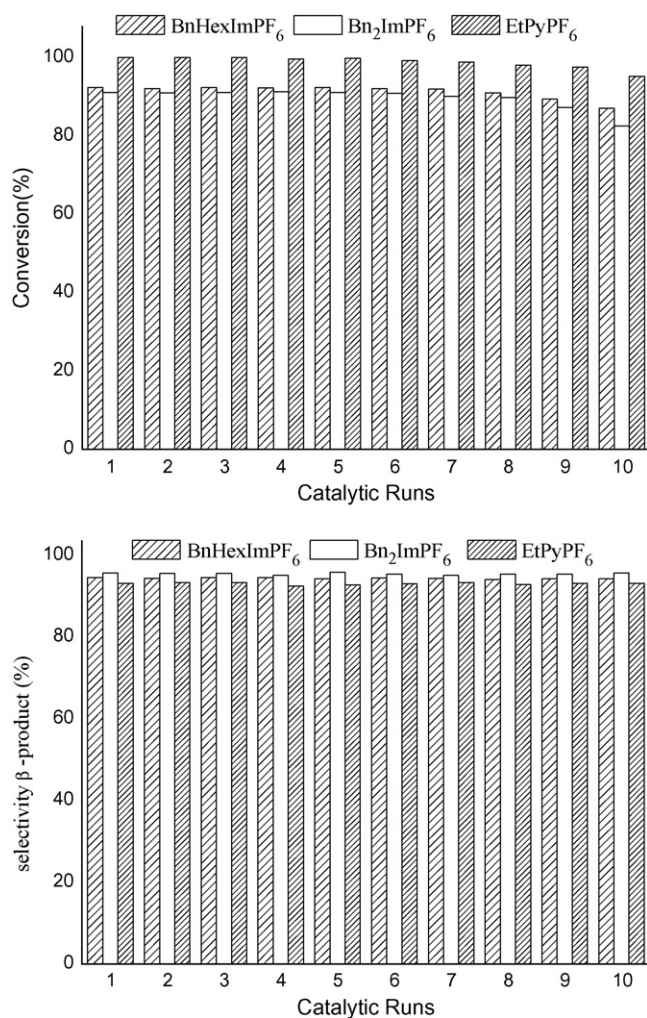


Fig. 1. Catalyst recycling.

### 3.4. Catalyst recycling experimental

Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/*N*-alkylpyridinium salt and Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/*N,N*-dialkylimidazolium salt are solids at room temperature and become liquid under reaction conditions. For each test cycle, products were decanted, leaving the catalyst at the bottom of the reaction vessel. In general, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/organic molten salts show excellent stability for the hydrosilylation reaction of styrene and triethoxysilane. For example, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/EtPyPF<sub>6</sub>, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/BnHexImPF<sub>6</sub> and Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/Bn<sub>2</sub>ImPF<sub>6</sub>, etc. catalysts can be reused more than 10 times without noticeable loss of catalytic activity and selectivity. The results of catalyst recycling measurements are shown in Fig. 1.

## 4. Conclusion

In summary, organic molten *N*-alkylpyridinium or *N,N*-dialkylimidazolium salts, which are solid at room temperature,

can be used as a support for transition metal catalysts. The organic molten salts are especially effective for improving the catalytic activity and selectivity of the Rh(PPh<sub>3</sub>)<sub>3</sub>Cl complex for hydrosilylation of alkenes and triethoxysilane. The substituents attached to the molten salt cation also have an impact on the catalytic process; the catalytic activities of the Rh(PPh<sub>3</sub>)<sub>3</sub>Cl/organic molten salt catalyst system decreased slightly with increasing length of the alkyl chain attached to the cation, while the ratio of β/α increased. By using *N*-alkylpyridinium or *N,N*-dialkylimidazolium-based ionic liquids (molten salts) as thermoregulated catalytic supports, a hydrosilylation process with the reaction conducted as a liquid–liquid biphas followed by a liquid–solid biphas for separation, can be designed.

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