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FULL PAPER

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Synthesis of novel poly(ethylene glycol)-containing imidazolium-functionalized phosphine ligands and their application in the hydrosilylation of olefins

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A series of polyethylene glycol-containing imidazolium-functionalized phosphine ligands (mPEG-im-PPh_2) were successfully synthesized and used in the rhodium-catalyzed hydrosilylation of olefins. The results indicate that the $RhCl_3$/mPEG-im-PPh_2 catalytic system exhibits both excellent activity and selectivity for the β-adduct. In addition, the catalytic system may be recycled at least six times.

KEYWORDS
diphenylphosphine salts, hydrosilylation, poly(ethylene glycol) (PEG)

1 | INTRODUCTION

Poly(ethylene glycol) (PEG) has attracted a great amount of interest as a reusable solvent medium for organic syntheses and catalytic processes because it is non-volatile, inexpensive and non-toxic. Furthermore, the properties of PEG can be tuned upon its modification with functional groups. Conjugates combining some of the properties of both the starting substrate and PEG can be produced when PEG is used as a covalent modifier for various substrates.

In homogeneous catalytic processes, in addition to the metal center used, the ligand also plays an important role in the reactions.[1–3] Generally, the electronic, geometric and steric properties of the ligands have a significant effect on the catalytic activity of their corresponding metal complexes. In particular, organic phosphine ligands have played a crucial role in transition metal catalysis. Numerous catalytic reactions, such as Wittig ylide formation,[4,5] Mukaiyama aldol reaction[6,7] and Mitsunobu reaction,[8–10] have been intensively developed along with thorough research on transition metal complexes coordinated with organic phosphine ligands.[11–13]

The hydrosilylation of alkenes is one of the most important methods used for the preparation of organosilicon compounds. It has been reported that the hydrosilylation of alkynes or alkenes can be effectively catalyzed using Wilkinson's catalyst ($Rh(PPh_3)_3Cl$).[14,15] In this catalytic process, the organic phosphine ligands play a significant role in the hydrosilylation reaction.[16–20] A series of rhodium catalysts with PEG-based ionic liquids have been used as efficient and recyclable catalyst systems for hydrosilylation reactions.[21,22]

In the present paper, we report the preparation of PEG-containing imidazolium-functionalized phosphine ligands (mPEG-im-PPh_2) and their application in the rhodium-catalyzed hydrosilylation of olefins.

2 | EXPERIMENTAL

2.1 | General

Styrene was washed with 5% NaOH and dried with Na_2SO_4. After filtration, the styrene was distilled under reduced pressure. All other substances were purchased from Aldrich and were used as received.

Gas chromatography: Trace DSQ GC column = DB-5 30 m × 2.5 mm × 0.25 μm, split = 50:1, flow = 1 ml min^{-1} constant flow, inlet temperature = 260 °C, column temperature = 50 °C (hold 1 min) then 15 °C min^{-1} up to 260 °C (hold 10 min).

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured using a Bruker AV400 spectrometer operating at 400.13, 100.62 and 161.97 MHz, respectively. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were recorded in ppm relative to residual proton of deuterated dimethylsulfoxide (DMSO-d_6) (^{1}H, 2.50 ppm; ^{13}C 39.5 ppm). ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 external standard.

2.2 | Preparation of mPEG-im-PPh_2

Monomethoxy PEG (0.1 mol) was dissolved in toluene (100 ml) in a 250 ml three-necked flask and the stirred solution was heated at reflux for 2 h to remove the water contained in the PEG by azeotropic dehydration. After cooling, dried pyridine (0.125 mol) was added to the solution and then thionyl chloride (0.125 mol) was added dropwise with stirring. The color of the solution changed from faint yellow to reddish brown. The reaction mixture was stirred for 24 h at 80 °C. After cooling to room temperature, a mixture of hydrochloric acid (8 ml) and water (16 ml) was added and stirred, and the layers were allowed to separate, and the lower layer was twice extracted with toluene. The extracts were combined with the upper organic phase and the solvent was removed under vacuum to afford monomethoxy PEG chloride. A mixture of monomethoxy PEG chloride (10.0 mmol) and 1-alkylimidazole (11.0 mmol) was diluted in 1,1,1-trichloroethane (10.0 ml), and the solution was refluxed for 36 h and the phases were separated. The lower phase was washed twice with 5 ml of 1,1,1-trichloroethane and once with 10.0 ml of ethyl ether. Residual solvents were removed by rotary evaporation. Removal of the solvent under vacuum afforded a yellow oil (mPEGBImCl). A solution of $LiPPh_2$, freshly prepared from Li (0.8 g, 0.11 mol) and PPh_3 (13.1 g, 0.05 mol), in tetrahydrofuran (THF; 50 ml), was added to a solution of mPEGBImCl (0.05 mol) in THF (50 ml). The mixture was stirred for 1 h at room temperature, then the supernatant was decanted off and the remaining solid mPEG-im-PPh_2 was washed with toluene (2 × 15 ml) and dried *in vacuo*. The synthesis route is shown in Scheme 1.

1a Yield: 88.0%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.24 (s, 1H, imidazol), 7.66 (s, 1H, imidazol), 7.51–7.76 (m, 10H, Ph), 4.31 (m, 2NCH_2), 3.81 (s, 3H, NCH_3), 3.72 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.21 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.5 (imidazol), 139.7 (Ph), 132.5 (Ph), 128.9 (Ph), 125.1 (Ph), 123.4 (imidazol), 123.2 (imidazol), 68.7 (NCH_2CH_2O), 59.1 (OCH_3), 49.3 (NCH_2CH_2O), 36.5 (NCH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −31.5.

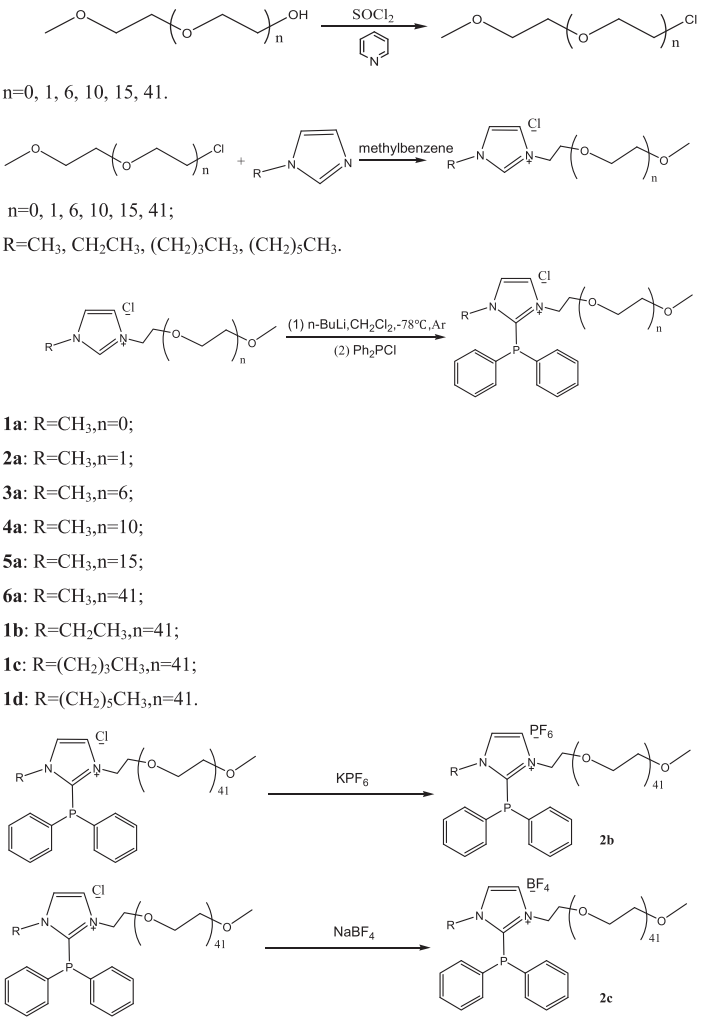
2a Yield: 85.7%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.97 (s, 1H, imidazol), 7.67 (s, 1H, imidazol), 7.50–7.77 (m, 10H, Ph), 4.33 (m, 2NCH_2), 3.87 (s, 3H, NCH_3), 3.71 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.51 (s, 4H, (OCH_2CH_2)), 3.21 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.1 (imidazol), 139.7 (Ph), 132.5 (Ph), 128.1 (Ph), 125.1 (Ph), 123.8 (imidazol), 123.2 (imidazol), 69.4 (CH_2CH_2O), 68.1 (NCH_2CH_2O), 59.1 (OCH_3), 49.5 (NCH_2CH_2O), 35.9 (NCH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −31.8.

3a Yield: 86.1%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.91 (s, 1H, imidazol), 7.64 (s, 1H, imidazol), 7.51–7.76 (m, 10H, Ph), 4.30 (m, 2NCH_2), 3.80 (s, 3H, NCH_3), 3.75 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.53 (s, (OCH_2CH_2)$_6$), 3.21 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.6 (imidazol), 139.3 (Ph), 132.8 (Ph), 128.0 (Ph), 125.1 (Ph), 123.5 (imidazol), 123.4 (imidazol), 69.5 ((CH_2CH_2O)$_6$), 68.1 (NCH_2CH_2O), 59.1 (OCH_3), 49.3 (NCH_2CH_2O), 36.7 (NCH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −33.1.

4a Yield: 84.7%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.89 (s, 1H, imidazol), 7.67 (s, 1H, imidazol), 7.49–7.77 (m, 10H, Ph), 4.31 (m, 2H, 2NCH_2), 3.83 (s, 3H, NCH_3), 3.77 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.50 (s, (OCH_2CH_2)$_{10}$), 3.23 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 140.6 (imidazol), 139.1 (Ph), 132.3 (Ph), 128.4 (Ph), 125.7 (Ph), 123.1 (imidazol), 123.5 (imidazol), 69.1 ((CH_2CH_2O)$_{10}$), 67.9 (NCH_2CH_2O), 58.1 (OCH_3), 45.3 (NCH_2CH_2O), 35.7 (NCH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −33.9.

5a Yield: 83.6%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.93 (s, 1H, imidazol), 7.67 (s, 1H, imidazol), 7.51–7.73 (m, 10H, Ph), 4.31 (m, 2NCH_2), 3.85 (s, 3H, NCH_3), 3.73 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.51 (s, (OCH_2CH_2)$_{15}$), 3.25 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.7 (imidazol), 139.3 (Ph), 132.9 (Ph), 128.3 (Ph), 125.1 (Ph), 123.7 (imidazol), 123.1 (imidazol), 69.1 ((CH_2CH_2O)$_{15}$), 68.5 (NCH_2CH_2O), 59.3 (OCH_3), 49.1 (NCH_2CH_2O), 36.7 (NCH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −34.7.

6a Yield: 83.1%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.91 (s, 1H, imidazol), 7.61 (s, 1H, imidazol),



SCHEME 1 Synthesis of 2-diphenylphosphine Polyethylene-glycol functionalized imidazolium (mPEG-im-PPh_2)

7.51–7.73 (m, 10H, Ph), 4.33 (m, 2NCH_2), 3.87 (s, 3H, NCH_3), 3.71 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.51 (s, (OCH_2CH_2)$_{41}$), 3.23 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.3 (imidazol), 139.1 (Ph), 132.7 (Ph), 128.1 (Ph), 125.3 (Ph), 123.9 (imidazol), 123.3 (imidazol), 69.7 ((CH_2CH_2O)$_{41}$), 68.5 (NCH_2CH_2O), 59.1 (OCH_3), 49.3 (NCH_2CH_2O), 36.3 (NCH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −35.9.

1b Yield: 81.1%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.93 (s, 1H, imidazol), 7.67 (s, 1H, imidazol), 7.51–7.73 (m, 10H, Ph), 4.63 (m, 2H, NCH_2), 4.31 (m, 2H, NCH_2), 3.73 (t, J = 8 Hz, 2H, OCH_2CH_2N), 3.55 (s, (OCH_2CH_2)$_{41}$), 3.23 (s, 3H, OCH_3), 0.84 (t, J = 8 Hz, 3H, CH_3CH$_2$N). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.1 (imidazol), 138.1 (Ph), 133.7 (Ph), 127.1 (Ph), 126.3 (Ph), 125.9 (imidazol), 123.3 (imidazol), 69.1 ((CH_2CH_2O)$_{41}$), 68.3 (NCH_2CH_2O), 59.3 (OCH_3), 49.1 (NCH_2CH_2O), 45.3 (NCH_2), 15.9 (NCH_2CH_3). ^{31}P NMR (DMSO-d_6, δ, ppm): −36.3.

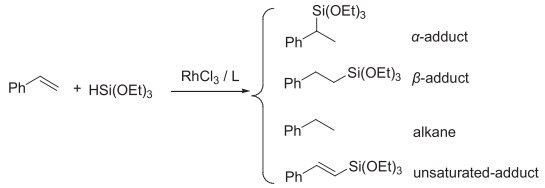
1c Yield: 80.3%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.87 (s, 1H, imidazol), 7.73 (s, 1H, imidazol), 7.51–7.79 (m, 10H, Ph), 4.61 (m, 2H, NCH_2), 4.23 (m, 2H, NCH_2), 3.71 (t, J = 8 Hz, 2H, OCH_2CH$_2$N), 3.54 (s, (OCH_2CH_2)$_{41}$), 3.21 (s, 3H, OCH_3), 1.31–1.89 (m, 4H, CH$_2$), 0.89 (t, J = 8 Hz, 3H, CH_3C$_3$H$_6$N). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.3 (imidazol), 138.9 (Ph), 133.4 (Ph), 127.3 (Ph), 126.1 (Ph), 125.7 (imidazol), 123.1 (imidazol), 69.7 ((CH_2CH_2O)$_{41}$), 68.1 (NCH_2CH_2O), 59.7 (OCH_3), 49.1 (NCH_2CH_2O), 50.2 (NCH_2), 31.7, 19.1 (CH_3C$_2$H$_4$CH$_2$N), 13.8 (CH$_3$C$_2$H$_4$CH$_2$N). ^{31}P NMR (DMSO-d_6, δ, ppm): −36.9.

1d Yield: 80.1%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.89 (s, 1H, imidazol), 7.65 (s, 1H, imidazol), 7.47–7.77 (m, 10H, Ph), 4.65 (m, 2H, NCH_2), 4.19 (m, 2H, NCH_2), 3.73 (t, J = 8 Hz, 2H, OCH_2CH$_2$N), 3.55 (s, (OCH_2CH_2)$_{41}$), 3.27 (s, 3H, OCH_3), 1.29–1.67 (m, 8H, CH$_2$), 0.86 (t, J = 8 Hz, 3H, CH_3C$_3$H$_6$N). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.1 (imidazol), 139.0 (Ph), 133.7 (Ph), 127.9 (Ph), 126.5 (Ph), 125.9 (imidazol), 123.3 (imidazol), 69.9 ((CH_2CH_2O)$_{41}$), 68.7 (NCH_2CH_2O), 59.7 (OCH_3), 49.5 (NCH_2CH_2O), 50.1 (NCH_2), 22.3, 29.8, 30.4, 31.0 (CH_3C$_4$H$_8$CH$_2$N), 14.1 (CH$_3$C$_2$H$_4$CH$_2$N). ^{31}P NMR (DMSO-d_6, δ, ppm): −37.1.

The solid **6a** (0.05 mol) was dissolved in 15 ml of water and then mixed with KPF_6 (0.06 mol) in 10 ml of water. The mixture was stirred for 24 h at room temperature. After decantation, the crude product was washed twice with 20 ml of water and dried under vacuum. Product **2b** was obtained.

2b Yield: 53.4%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.21 (s, 1H, imidazol), 7.89 (s, 1H, imidazol), 7.49–7.77 (m, 10H, Ph), 4.31 (m, 2NCH_2), 3.85 (s, 3H, NCH_3), 3.69 (t, J = 8 Hz, 2H, OCH_2CH$_2$N), 3.48 (s, (OCH_2CH_2)$_{41}$), 3.22 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 141.9 (imidazol), 132.9 (Ph), 132.5 (Ph), 128.3 (Ph), 125.1 (Ph), 123.4 (imidazol), 123.1 (imidazol), 69.9 ((CH$_2$CH$_2$O)$_{41}$), 68.7 (NCH$_2$CH$_2$O), 59.3 (OCH$_3$), 49.1 (NCH$_2$CH$_2$O), 36.7 (NCH$_3$). ^{31}P NMR (DMSO-d_6, δ, ppm): −39.7, −143.0 (PF_6^-, J = 706.8 Hz).

The solid **6a** (0.05 mol) was dissolved in 15 ml of acetone and then mixed with $NaBF_4$ (0.06 mol) in 10 ml of acetone. The mixture was stirred for 24 h at room temperature. After decantation, the crude product was diluted in 30 ml of methylene chloride, washed twice with 20 ml of water and dried under vacuum. Product **2c** was obtained.



SCHEME 2 The hydrosilylation reaction of alkenes catalyzed

2c Yield: 37.1%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.82 (s, 1H, imidazol), 8.67 (s, 1H, imidazol), 7.50–7.75 (m, 10H, Ph), 4.32 (m, 2NCH_2), 3.84 (s, 3H, NCH_3), 3.69 (t, J = 8 Hz, 2H, OCH_2CH$_2$N), 3.51 (s, (OCH_2CH_2)$_{41}$), 3.22 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 142.3 (imidazol), 139.7 (Ph), 132.1 (Ph), 128.5 (Ph), 125.1 (Ph), 123.3 (imidazol), 123.1 (imidazol), 69.9 ((CH$_2$CH$_2$O)$_{41}$), 68.3 (NCH$_2$CH$_2$O), 59.7 (OCH$_3$), 49.1 (NCH$_2$CH$_2$O), 36.1 (NCH$_3$). ^{31}P NMR (DMSO-d_6, δ, ppm): −36.7.

2.3 | Catalytic Hydrosilylation of Alkene with Triethoxysilane

A 10 ml three-necked flask equipped with a magnetic stirrer was charged with $RhCl_3 \cdot 3H_2O$ (8.0×10^{-3} mmol) and phosphine ligand (4.0×10^{-2} mmol) under argon atmosphere. Then alkene (4 mmol) and silane (4.87 mmol) were added via syringe. The hydrosilylation reaction (Scheme 2) was conducted with constant stirring at an appropriate temperature for 5 h. At the end of the reaction, the conversion of alkene and the selectivity of product were determined using GC.

3 | RESULTS AND DISCUSSION

3.1 | Effect of Length of PEG Chain on Hydrosilylation Reaction

The catalytic properties of $RhCl_3$/mPEG-im-PPh_2 in the hydrosilylation reaction of styrene with triethoxysilane were investigated, and the results are listed in Table 1.

TABLE 1 Effect of molecular weight on hydrosilylation catalyzed with $RhCl_3$[a]

			Selectivity (%)			
Entry	**Ligand**	**Conv. (%)**	**β**	**α**	**Ethylbenzene**	**Dehydrogenative silylation**
1	—	85.2	57.8	22.2	13.0	7.0
2	**1a**	95.1	70.1	17.1	7.4	5.4
3	**2a**	95.9	75.4	13.2	6.3	5.1
4	**3a**	94.2	80.3	12.1	3.4	4.2
5	**4a**	93.8	82.5	9.8	3.3	4.4
6	**5a**	93.5	85.6	6.8	3.1	4.5
7	**6a**	91.1	90.4	2.3	2.6	4.7
8	**1b**	89.9	87.1	2.1	6.3	4.5
9	**1c**	87.2	86.1	1.9	7.8	4.2
10	**1d**	86.5	86.4	1.1	8.6	3.9
11	**2b**	93.4	92.1	1.5	2.8	3.6
12	**2c**	82.4	90.3	2.2	2.6	4.9

[a]Reaction conditions: styrene 4.0 mmol, $(EtO)_3SiH$ 4.4 mmol, 5 h, 70 °C, $RhCl_3$ 0.001 mmol, $n(RhCl_3)$:n(mPEG-im-PPh_2) = 1:3.

An 85.2% conversion of styrene and 57.8% selectivity for the β-adduct were obtained in the absence of a phosphine ligand (Table 1, entry 1). When $RhCl_3$ was mixed with mPEG-im-PPh_2, it exhibited enhanced catalytic activity and selectivity (Table 1, entries 2–7). In addition, it was found that the catalytic activity of $RhCl_3$/mPEG-im-PPh_2 decreased slightly upon increasing the length of the PEG chain. In contrast, the ratio of the β-adduct to α-adduct (β/α) clearly increased. When $RhCl_3$/**6a** was used as the catalyst, the β-adduct selectivity improved to 90.4% (Table 1, entry 7). The results demonstrate that mPEG-im-PPh_2 is an effective promoter in the rhodium-catalyzed hydrosilylation reaction.

The effect of the length of the alkyl chain in the imidazolium ring was investigated. When $RhCl_3$ was mixed with mPEG-im-PPh_2 (**6a**, **1b**, **1c** and **1d**), it exhibited higher catalytic activity and β-adduct selectivity. At the same time, the catalytic activity of the $RhCl_3$/mPEG-im-PPh_2 (**6a**, **1b**, **1c** and **1d**) catalysts slightly decreased upon increasing the length of the alkyl chain in the imidazolium ring, while the ratio of the β-adduct to the α-adduct (β/α) slightly increased (Table 1, entries 7–10). This demonstrates that the substituents on the imidazolium ring have a significant impact on the catalytic process. Different substituents attached to the cation result in different steric hindrance observed at the catalytic center.

The effect of the anion in the imidazolium was investigated. When $RhCl_3$ was mixed with mPEG-im-PPh_2 (**2b**), it exhibited enhanced catalytic activity and β-adduct selectivity when compared to **6a**. When $RhCl_3$ was mixed with mPEG-im-PPh_2 (**2c**), it exhibited a lower catalytic activity than with **6a**. However, due to the complexity of the preparation process, the separation yield of **2b** was low. Therefore, **6a** was selected as the representative catalyst.

3.2 | Effect of Amount of mPEG-im-PPh_2 on Hydrosilylation Reaction

The effect of the amount of mPEG-im-PPh_2 on the hydrosilylation reaction was also investigated, and the results are listed in Table 2. The conversion of styrene and the β-adduct selectivity were 90.7 and 81.6% using the catalyst with a ratio of n(mPEG-im-PPh_2):n($RhCl_3$) = 1:1 (Table 2, entry 2). When the ratio of n(mPEG-im-PPh_2):n($RhCl_3$) = 5:1, the conversion of styrene and the β-adduct selectivity were 94.7 and 90.5%, respectively (Table 2, entry 4). This shows that a certain amount of mPEG-im-PPh_2 ligand was conducive to improving the catalytic activity. Upon increasing the ratio from 5:1 to 80:1, the conversion of styrene and the β-adduct selectivity decreased (Table 2, entries 4–8). This suggests that too many ligands around the Rh center have a negative impact on the catalytic activity.

3.3 | Catalyst Recycling

In general, $RhCl_3$/mPEG-im-PPh_2 shows excellent stability in the hydrosilylation reaction of styrene and triethoxysilane. For example, the $RhCl_3$/**6a** catalyst system can be reused more than six times without any noticeable loss in the catalytic activity and selectivity. The results of the catalyst recycling experiments are shown in Figure 1.

3.4 | Hydrosilylation Reaction of Other Aliphatic Alkenes

When aliphatic alkenes such as 1-hexene, 1-octene, (vinyloxy)butane and ethoxyethene were used as the substrates in the hydrosilylation reaction, excellent conversions and selectivities were obtained with the $RhCl_3$/**6a** catalyst system (Table 3).

TABLE 2 Effect of amount of **6a** on hydrosilylation catalyzed with $RhCl_3$[a]

			Selectivity (%)			
Entry	Ligand	Conv. (%)	β	α	Ethylbenzene	Dehydrogenative silylation
1	—	85.2	57.8	22.2	13.0	7.0
2	1:1	90.7	81.6	6.3	5.2	6.9
3	3:1	91.1	90.4	2.3	2.6	4.7
4	5:1	94.7	90.5	3.4	2.2	3.9
5	8:1	89.9	77.3	6.6	10.2	5.9
6	25:1	73.8	70.4	9.1	10.8	9.7
7	40:1	63.6	67.7	11.2	10.5	10.6
8	80:1	55.6	64.5	15.7	10.7	9.1

[a]Reaction conditions: styrene 4.0 mmol, $(EtO)_3SiH$ 4.4 mmol, 5 h, 70 °C, $RhCl_3$ 0.001 mmol.

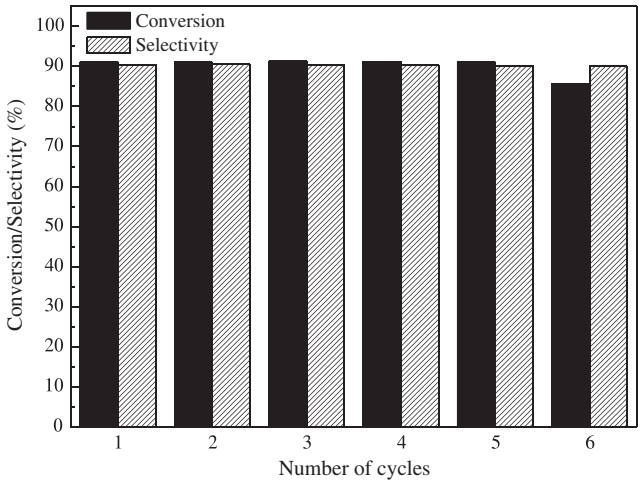


FIGURE 1 Reuse of $RhCl_3$/**6a** catalytic system. (Reaction conditions: styrene, 4.0 mmol; $(EtO)_3SiH$, 4.4 mmol; 5 h; 70 °C; $n(RhCl_3)$:n(mPEG-im-PPh_2) = 1:5; $RhCl_3$, 0.001 mmol)

TABLE 3 Hydrosilylation of alkene and triethoxysilane catalyzed with $RhCl_3$/**6a**[a]

			Selectivity (%)		
Entry	Substrate	Conv. (%)	β	α	Other
1	$CH_3(CH_2)_3CH{=}CH_2$	99.2	>99.9	—	—
2	$CH_3(CH_2)_5CH{=}CH_2$	98.8	>99.9	—	—
3	$CH_3(CH_2)_3OCH{=}CH_2$	99.8	>99.9	—	—
4	$CH_3CH_2OCH{=}CH_2$	99.9	>99.9	—	—

[a]Reaction conditions: styrene 4.0 mmol, $(EtO)_3SiH$ 4.4 mmol, 5 h, 70 °C, $n(RhCl_3)$:n(mPEG-im-PPh_2) = 1:5, $RhCl_3$ 0.001 mmol.

4 | CONCLUSIONS

In summary, a series of mPEG-im-PPh_2 ligands have been successfully synthesized and used in the hydrosilylation reaction of alkenes catalyzed using the $RhCl_3$/mPEG-im-PPh_2 catalyst system. The $RhCl_3$/mPEG-im-PPh_2 catalyst showed excellent activity and selectivity for the β-adduct. The catalytic system can be recycled six times without any noticeable loss in catalytic activity and selectivity.

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