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Hydrosilylation reactions catalyzed by rhodium complexes with phosphine ligands functionalized with imidazolium salts

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ABSTRACT

Hydrosilylation reactions of styrene with triethoxysilane catalyzed by rhodium complexes with phosphine ligands functionalized with imidazolium salts are reported. In comparison with Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, all of the present rhodium complexes with phosphines functionalized with imidazolium salts exhibit higher catalytic activity and selectivity.

1. Introduction

Hydrosilylation processes, particularly of carbon–carbon multiple bonds, have been extensively applied in the fields of organic synthesis and material science in the last two decades [1–3]. Although a wide range of catalysts has been tested for hydrosilylation, most research and industrial syntheses have been carried out in the presence of platinum complexes or rhodium complexes. Phosphine complexes of rhodium effectively catalyze the hydrosilylation of 1-alkenes [3–6]. In this catalytic process, besides the Rh center used, the phosphine ligands also play an important role in the hydrosilylation [7]. The primary role of the phosphines is to support the metal in the form of stable species that can subsequently enter the catalytic cycle and thereby help prevent the formation of inactive metal aggregates. On the other hand, room temperature ionic liquids (ILs), which are entirely constituted of ions, have attracted great interest as novel and environmentally friendly benign media and catalyst systems [8,9]. Moreover, the physical and chemical properties of dialkylimidazolium salts can also be specifically altered by changing the attached substituents and/or associated anions. There have been a few examples of hydrosilylations with the use of ionic liquids [10–13]. Recently, our group [7,14] has reported that $Rh(PPh_3)_3Cl$/IL (molten salt) may be used in the hydrosilylation process as a thermoregulated and recyclable catalyst system that combines the advantages of an IL and convenient product separation. The substituents attached to the cation of the molten salt were found to have an impact on the catalytic process [7,14]. On the other hand, our studies have also revealed that phosphines with 2-imidazolium ligands (Scheme 1) enhance the catalytic activity and selectivity of rhodium complexes for hydrosilylation reactions [15]. Consequently, it was speculated that phosphines functionalized with ionic liquids might be good candidates as ligands for rhodium-catalyzed hydrosilylation reactions. For the present study, we have synthesized several phosphine ligands functionalized with imidazolium salts (Scheme 2), and the application of these ligands in the rhodium-catalyzed hydrosilylation of styrene with silanes has been investigated.

2. Experimental

2.1. General methods

Styrene was washed with 5% aqueous NaOH solution 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. All reactions were carried out under a dry argon atmosphere using Schlenk glassware and vacuum-line techniques. Solvents for synthesis were dried and degassed by standard methods before use.

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

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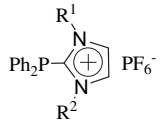


R^1: CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}

R^2: C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}

Scheme 1. 2-Imidazolium phosphines.

flow, inlet temperature: 260 °C, column temperature: 50 °C (hold 1 min) then 15 °C min^{-1} up to 260 °C (hold 10 min).

^1H, ^{13}C and ^{31}P NMR spectra were measured using a Bruker AV400 spectrometer operating at 400.13 MHz, 100.62 MHz and 161.97 MHz, respectively. Chemical shifts for ^1H and ^{13}C spectra are given in ppm relative to the residual proton signal of [d_6] DMSO (^1H: δ 2.50; ^{13}C: δ 39.5). ^{31}P NMR chemical shifts are specified relative to 85% H_3PO_4 as an external standard.

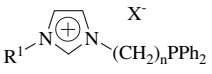
2.2. Synthesis of imidazolium salts

2.2.1. General procedure for the synthesis of **1b**–**8b**

A solution of the appropriate N-substituted imidazole (0.05 mol) in tetrahydrofuran (THF; 20 mL) was treated with a solution of an equivalent amount of $Br(CH_2)_nCl$ (0.05 mol) in THF (20 mL). The mixture was stirred at 50 °C for 12 h. During this time, a cream-colored solid precipitated in the flask. The suspension was cooled to room temperature, the supernatant was decanted off, and the solid was washed with THF (2 × 15 mL). A white solid was obtained.

The white solid obtained (0.03 mol) was dissolved in H_2O (30 mL) and this solution was treated with a solution of NH_4PF_6 (0.033 mol) in H_2O (10 mL). The resulting mixture was stirred for 2 h at room temperature. After decanting the supernatant, the oil salt was diluted with dichloromethane (30 mL), and this solution was washed with H_2O (2 × 20 mL) and dried over anhydrous magnesium sulfate. Removal of the solvent under vacuum afforded a white solid. All of the prepared compounds showed spectroscopic data (^1H NMR and ^{13}C NMR) in accordance with the proposed structures (**1b**–**7b**).

The white solid (0.03 mol) obtained as described above was dissolved in acetone (30 mL) and this solution was treated with a solution of $NaBF_4$ (0.033 mol) in acetone (10 mL). The resulting mixture was stirred for 2 h at room temperature. The white precipitate was then collected by filtration, the solvent was removed under vacuum, and the solid was dissolved in dichloromethane (30 mL). This solution was washed with H_2O (2 × 20 mL) and dried over anhydrous magnesium sulfate. Removal of the solvent under vacuum afforded a white solid. The prepared compound showed spectroscopic data (^1H NMR and ^{13}C NMR) in accordance with the assigned structure (**8b**).



1c: R^1=CH_3, n=2, X=PF_6^-

2c: R^1=C_4H_9, n=2, X=PF_6^-

3c: R^1=C_6H_{13}, n=2, X=PF_6^-

4c: R^1=C_8H_{17}, n=2, X=PF_6^-

5c: R^1=C_8H_{17}, n=3, X=PF_6^-

6c: R^1=C_8H_{17}, n=4, X=PF_6^-

7c: R^1=C_8H_{17}, n=5, X=PF_6^-

8c: R^1=C_8H_{17}, n=2, X=BF_4^-

Scheme 2. Phosphine ligands functionalized with ionic liquids.

2.2.2. 1-(2-Chloroethyl)-3-methylimidazolium hexafluorophosphate (**1b**)

^1H NMR (DMSO-d_6) δ (ppm): 3.43 (m, 3H, CH_3), 3.83 (t, J = 8 Hz, 2H, CH_2Cl), 4.57 (m, 2H, NCH_2), 7.56 (brs, 1H, imidazol), 7.74 (brs, 1H, imidazol), 8.95 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 36.9 (NCH_3), 42.1($ClCH_2$), 49.5(NCH_2), 122.7(imidazol), 123.2(imidazol), 137.1 (imidazol). Anal. Calc. for **1b** ($C_6H_{10}ClF_6N_2P$): C, 24.80; H, 3.47; N, 9.64. Found: C, 24.75; H, 3.43; N, 9.61. Yield: 85%

2.2.3. 1-(2-Chloroethyl)-3-butylimidazolium hexafluorophosphate (**2b**)

^1H NMR (DMSO-d_6) δ (ppm): 0.89 (t, J = 8 Hz, 3H, CH_3), 1.31–1.89 (m, 4H, CH_2), 4.07 (t, J = 8 Hz, 2H, CH_2Cl), 4.37 (m, 2H, NCH_2), 4.64 (m, 2H, NCH_2), 7.74 (brs, 1H, imidazol), 7.81 (brs, 1H, imidazol), 9.17 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.8(CH_3), 19.3 (CH_2), 33.1 (CH_2), 41.9 ($ClCH_2$), 49.2 (NCH_2), 50.2 (NCH_2), 122.1 (imidazol), 123.3 (imidazol), 136.8 (imidazol). Anal. Calc. for **2b** ($C_9H_{16}ClF_6N_2P$): C, 32.50; H, 4.85; N, 8.42. Found: C, 32.40; H, 4.84; N, 8.41. Yield: 81%

2.2.4. 1-(2-Chloroethyl)-3-hexylimidazolium hexafluorophosphate (**3b**)

^1H NMR (DMSO-d_6) δ (ppm): 0.84 (t, J = 8 Hz, 3H, CH_3), 1.34–1.62 (m, 8H, CH_2), 4.19 (t, J = 8 Hz, 2H, CH_2Cl), 4.23 (m, 2H, NCH_2), 4.85 (m, 2H, NCH_2), 7.74 (brs, 1H, imidazol), 7.83 (brs, 1H, imidazol), 9.23 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.3 (CH_3), 22.1(CH_2), 29.7 (CH_2), 30.4 (CH_2), 31.2 (CH_2), 42.1($ClCH_2$), 50.1 (NCH_2), 50.4 (NCH_2), 123.1 (imidazol), 124.1 (imidazol), 136.3 (imidazol). Anal. Calc. for **3b** ($C_{11}H_{20}ClF_6N_2P$): C, 36.63; H, 5.59; N, 7.77. Found: C, 36.61; H, 5.59; N, 7.72. Yield: 83%.

2.2.5. 1-(2-Chloroethyl)-3-octylimidazolium hexafluorophosphate (**4b**)

^1H NMR (DMSO-d_6) δ (ppm): 0.82 (t, J = 8 Hz, 3H, CH_3), 1.22–1.83 (m, 12H, CH_2), 4.12 (m, 2H, NCH_2), 4.21 (t, J = 8 Hz, 2H, CH_2Cl), 4.95 (m, 2H, NCH_2), 7.67 (brs, 1H, imidazol), 7.91 (brs, 1H, imidazol), 8.97 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.1(CH_3), 22.8 (CH_2), 25.9(CH_2), 28.2 (CH_2), 30.5 (CH_2), 31.6(CH_2), 31.7 (CH_2), 42.1 ($ClCH_2$), 50.3 (NCH_2), 50.5 (NCH_2), 122.2 (imidazol), 123.5 (imidazol), 137.1 (imidazol). Anal. Calc. for **4b** ($C_{13}H_{24}ClF_6N_2P$): C, 40.16; H, 6.22; N, 7.21. Found: C, 40.11; H, 6.21; N, 7.19. Yield: 78%

2.2.6. 1-(3-Chloropropyl)-3-octylimidazolium hexafluorophosphate (**5b**)

^1H NMR (DMSO-d_6) δ (ppm): 0.83 (t, J = 8 Hz, 3H, CH_3), 1.21–1.83 (m, 12H, CH_2), 2.63 (q, J = 4 Hz, 2H, CH_2), 3.84 (t, J = 8 Hz, 2H, CH_2Cl), 4.21–4.56 (m, 4H, NCH_2), 7.56 (brs, 1H, imidazol), 7.81 (brs, 1H, imidazol), 9.19 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.1 (CH_3), 22.7 (CH_2), 25.7 (CH_2), 28.1 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 34.0 (CH_2), 41.9 ($ClCH_2$), 49.8 (NCH_2), 50.3 (NCH_2), 122.1 (imidazol), 122.4 (imidazol), 136.8 (imidazol). Anal. Calc. for **5b** ($C_{14}H_{26}ClF_6N_2P$): C, 41.75; H, 6.51; N, 6.95. Found: C, 41.73; H, 6.48; N, 6.95. Yield: 75%.

2.2.7. 1-(4-Chlorobutyl)-3-octylimidazolium hexafluorophosphate (**6b**)

^1H NMR (DMSO-d_6) δ (ppm): 0.79 (t, J = 8 Hz, 3H, CH_3), 1.23–2.07 (m, 16H, CH_2), 3.88 (t, J = 8 Hz, 2H, CH_2Cl), 4.23–4.26 (m,

4H, NCH_2), 7.63 (brs, 1H, imidazol), 8.01 (brs, 1H, imidazol), 9.23 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.3 (CH_3), 22.4 (CH_2), 25.8 (CH_2), 26.1 (CH_2), 28.3 (CH_2), 30.2 (CH_2), 30.9 (CH_2), 31.5 (CH_2), 31.9 (CH_2), 43.9 ($ClCH_2$), 49.9 (NCH_2), 50.7 (NCH_2), 122.3 (imidazol), 123.4 (imidazol), 136.8 (imidazol). Anal. Calc. for **6b** ($C_{15}H_{28}ClF_6N_2P$): C, 43.22; H, 6.77; N, 6.72. Found: C, 43.18; H, 6.74; N, 6.71. Yield: 77%.

2.2.8. 1-(5-Chloropentyl)-3-octylimidazolium hexafluorophosphate (*7b*)

^1H NMR (DMSO-d_6) δ (ppm): 0.81 (t, J = 8 Hz, 3H, CH_3), 1.21–2.17 (m, 18H, CH_2), 3.81 (t, J = 8 Hz, 2H, CH_2Cl), 4.29–4.31 (m, 4H, NCH_2), 7.73 (brs, 1H, imidazol), 8.23 (brs, 1H, imidazol), 9.23 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.1 (CH_3), 22.8 (CH_2), 24.6 (CH_2), 26.8 (CH_2), 27.4 (CH_2), 28.3 (CH_2), 30.1 (CH_2), 30.7 (CH_2), 31.9 (CH_2), 32.8 (CH_2), 44.8 ($ClCH_2$), 50.1 (NCH_2), 50.5 (NCH_2), 122.3 (imidazol), 123.4 (imidazol), 137.1 (imidazol). Anal. Calc. for **7b** ($C_{16}H_{30}ClF_6N_2P$): C, 44.60; H, 7.02; N, 6.50. Found: C, 44.63; H, 7.05; N, 6.51. Yield: 73%.

2.2.9. 1-(2-Chloroethyl)-3-octylimidazolium tetrafluoroborate (*8b*)

^1H NMR (DMSO-d_6) δ (ppm): 0.81 (t, J = 8 Hz, 3H, CH_3), 1.32–1.89 (m, 12H, CH_2), 4.17 (t, J = 8 Hz, 2H, CH_2Cl), 4.57 (m, 2H, NCH_2), 4.81 (m, 2H, NCH_2), 7.61 (brs, 1H, imidazol), 7.87 (brs, 1H, imidazol), 9.12 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.9 (CH_3), 22.1 (CH_2), 26.1 (CH_2), 28.4 (CH_2), 30.3 (CH_2), 31.5 (CH_2), 31.9 (CH_2), 42.5 ($ClCH_2$), 50.6 (NCH_2), 50.9 (NCH_2), 123.2 (imidazol), 124.4 (imidazol), 138.2 (imidazol). Anal. Calc. for **8b** ($C_{13}H_{24}ClF_4N_2B$): C, 47.32; H, 7.32; N, 8.47. Found: C, 47.31; H, 7.31; N, 8.45. Yield: 71%.

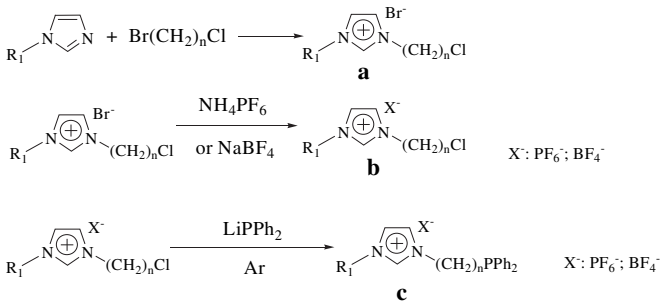
2.3. Synthesis of phosphines functionalized with imidazolium salts (Scheme 3)

2.3.1. General procedure for the synthesis of *1c*–*8c*

The ligands (**1c**–**8c**) employed in this study were prepared as shown in Scheme 3. 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 THF (50 mL), was added to a solution of the imidazolium salt (**1b**–**8b**) (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 was washed with toluene (2 × 15 mL) and dried in vacuo.

2.3.2. 1-(2-Diphenylphosphinoethyl)-3-methylimidazolium hexafluorophosphate (*1c*)

^1H NMR (DMSO-d_6) δ (ppm): 2.48 (t, J = 12 Hz, 2H, CH_2P), 3.82 (m, 3H, CH_3), 4.72 (m, 2H, NCH_2), 7.46–7.57 (m, 10H, Ph), 7.70 (brs, 1H, imidazol), 7.85 (brs, 1H, imidazol), 9.28 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 27.6(J_{P-C} = 8 Hz, PCH_2), 36.9 (NCH_3), 46.5 (J_{P-C} = 20 Hz, NCH_2), 122.7 (imidazol), 123.2 (imidazol), 127.5 (J_{P-C} = 6 Hz, PPh), 128.4 (J_{P-C} = 7 Hz, PPh), 129.5 (PPh), 132.3 (J_{P-C} = 13 Hz, PPh), 137.1 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −22.1, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **1c** ($C_{18}H_{20}F_6N_2P_2$): C, 49.10; H, 4.58; N, 6.36. Found: C, 49.05; H, 4.57; N, 6.37. Yield: 92%.



Scheme 3. Preparation of phosphine ligands functionalized with imidazolium salts.

2.3.3. 1-(2-Diphenylphosphinoethyl)-3-butylimidazolium hexafluorophosphate (*2c*)

^1H NMR (DMSO-d_6) δ (ppm): 0.87 (t, J = 8 Hz, 3H, CH_3), 2.54 (t, J = 12 Hz, 2H, CH_2P), 1.35–1.82 (m, 4H, CH_2), 4.39 (m, 2H, NCH_2), 4.61 (m, 2H, NCH_2), 7.41–7.49 (m, 10H, Ph), 7.71 (brs, 1H, imidazol), 7.89 (brs, 1H, imidazol), 9.34 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7 (CH_3), 19.1 (CH_2), 28.7 (J_{P-C} = 8 Hz, PCH_2), 33.4 (CH_2), 47.5 (J_{P-C} = 20 Hz, NCH_2), 50.8 (NCH_2), 123.1 (imidazol), 123.3 (imidazol), 128.2 (J_{P-C} = 6 Hz, PPh), 130.2 (J_{P-C} = 7 Hz, PPh), 130.8 (PPh), 133.2 (J_{P-C} = 13 Hz, PPh), 137.8 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −21.1, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **2c** ($C_{21}H_{26}F_6N_2P_2$): C, 52.29; H, 5.43; N, 5.81. Found: C, 52.30; H, 5.44; N, 5.83. Yield: 81%.

2.3.4. 1-(2-Diphenylphosphinoethyl)-3-hexylimidazolium hexafluorophosphate (*3c*)

^1H NMR (DMSO-d_6) δ (ppm): 0.83 (t, J = 8 Hz, 3H, CH_3), 1.31–1.63 (m, 8H, CH_2), 2.55 (t, J = 12 Hz, 2H, CH_2P), 4.21 (m, 2H, NCH_2), 4.39 (m, 2H, NCH_2), 7.36–7.49 (m, 10H, Ph), 7.84 (brs, 1H, imidazol), 7.91 (brs, 1H, imidazol), 9.37 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.2 (CH_3), 22.5 (CH_2), 28.7 (CH_2), 29.6 (J_{P-C} = 8 Hz, PCH_2), 30.2 (CH_2), 31.6 (CH_2), 48.7 (J_{P-C} = 20 Hz, NCH_2), 50.7 (NCH_2), 122.3 (imidazol), 122.8 (imidazol), 128.6(J_{P-C} = 6 Hz, PPh), 130.3 (J_{P-C} = 9 Hz, PPh), 130.8(PPh), 133.0(J_{P-C} = 14 Hz, PPh), 136.3 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −20.6, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **3c** ($C_{23}H_{30}F_6N_2P_2$): C, 54.12; H, 5.92; N, 5.49. Found: C, 54.09; H, 5.94; N, 5.47. Yield: 87%.

2.3.5. 1-(2-Diphenylphosphinoethyl)-3-octylimidazolium hexafluorophosphate (*4c*)

^1H NMR (DMSO-d_6) δ (ppm): 0.85 (t, J = 8 Hz, 3H, CH_3), 1.19–1.73 (m, 12H, CH_2), 2.56 (t, J = 12 Hz, 2H, CH_2P), 4.25 (m, 2H, NCH_2), 4.85 (m, 2H, NCH_2), 7.33–7.51 (m, 10H, Ph), 7.74 (brs, 1H, imidazol), 8.01 (brs, 1H, imidazol), 9.37 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.2 (CH_3), 22.4 (CH_2), 26.2 (CH_2), 28.1 (CH_2), 29.2 (J_{P-C} = 8 Hz, PCH_2), 30.5 (CH_2), 31.4 (CH_2), 31.7 (CH_2), 49.7 (J_{P-C} = 20 Hz, NCH_2), 51.2 (NCH_2), 122.3 (imidazol), 123.2 (imidazol), 128.9 (J_{P-C} = 7 Hz, PPh), 130.3 (J_{P-C} = 9 Hz, PPh), 131.0 (PPh), 132.8 (J_{P-C} = 12 Hz, PPh), 136.6 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −20.1, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **4c** ($C_{25}H_{34}F_6N_2P_2$): C, 55.76; H, 6.36; N, 5.20. Found: C, 55.71; H, 6.37; N, 5.23. Yield: 83%.

2.3.6. 1-(3-Diphenylphosphinopropyl)-3-octylimidazolium hexafluorophosphate (*5c*)

^1H NMR (DMSO-d_6) δ (ppm): 0.79 (t, J = 8 Hz, 3H, CH_3), 1.21–2.61 (m, 14H, CH_2), 2.87 (t, J = 12 Hz, 2H, CH_2P), 4.76 (m, 2H, NCH_2), 4.84 (m, 2H, NCH_2), 7.31–7.48 (m, 10H, Ph), 7.74 (brs, 1H, imidazol), 7.97 (brs, 1H, imidazol), 9.51 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.4 (CH_3), 22.8 (CH_2), 24.4 (J_{P-C} = 10 Hz, PCH_2CH_2), 25.9 (CH_2), 27.3 (J_{P-C} = 18 Hz, PCH_2CH_2), 28.3 (CH_2), 30.1 (CH_2), 31.6 (CH_2), 34.3 (CH_2), 50.6 (J_{P-C} = 19 Hz, NCH_2), 51.3 (NCH_2), 122.1 (imidazol), 123.4 (imidazol), 128.8 (J_{P-C} = 7 Hz, PPh), 130.8 (J_{P-C} = 9 Hz, PPh), 132.0 (PPh), 132.9 (J_{P-C} = 12 Hz, PPh), 137.6 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −17.1, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **5c** ($C_{26}H_{36}F_6N_2P_2$): C, 56.52; H, 6.57; N, 5.07. Found: C, 56.55; H, 6.57; N, 5.06. Yield: 81%.

2.3.7. 1-(4-Diphenylphosphinobutyl)-3-octylimidazolium hexafluorophosphate (*6c*)

^1H NMR (DMSO-d_6) δ (ppm): 0.79 (t, J = 8 Hz, 3H, CH_3), 1.21–2.09 (m, 16H, CH_2), 2.95 (t, J = 12 Hz, 2H, CH_2P), 4.44–4.61 (m,

4H, NCH_2), 7.33–7.47 (m, 10H, Ph), 7.83 (brs, 1H, imidazol), 7.94 (brs, 1H, imidazol), 9.09 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.3 (CH_3), 22.4 (CH_2), 25.1 (J_{P-C} = 10 Hz, $PCH_2CH_2CH_2$), 25.9 (CH_2), 28.1 (CH_2), 28.3 (J_{P-C} = 12 Hz, $PCH_2CH_2CH_2$), 30.5 (CH_2), 31.7 (CH_2), 32.5 (J_{P-C} = 12 Hz, $PCH_2CH_2CH_2$), 34.1 (CH_2), 51.1 (NCH_2), 52.5 (NCH_2), 122.6 (imidazol), 123.3 (imidazol), 128.9 (J_{P-C} = 7 Hz, PPh), 130.2 (J_{P-C} = 9 Hz, PPh), 131.8 (PPh), 132.3 (J_{P-C} = 12 Hz, PPh), 137.3 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −15.2, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **6c** ($C_{27}H_{38}F_6N_2P_2$): C, 57.24; H, 6.76; N, 4.94. Found: C, 57.26; H, 6.74; N, 4.99. Yield: 86%.

2.3.8. 1-(5-Diphenylphosphinopentyl)-3-octylimidazolium hexafluorophosphate (**7c**)

^1H NMR (DMSO-d_6) δ (ppm): 0.77 (t, J = 8 Hz, 3H, CH_3), 1.21–2.19 (m, 18H, CH_2), 2.97 (t, J = 12 Hz, 2H, CH_2P), 4.23–4.35 (m, 4H, NCH_2), 7.26–7.45 (m, 10H, Ph), 7.56 (brs, 1H, imidazol), 7.61 (brs, 1H, imidazol), 8.87 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.1 (CH_3), 22.5 (CH_2), 25.7 (CH_2), 27.3 (J_{P-C} = 10 Hz, $PCH_2CH_2CH_2$), 28.1 (CH_2), 28.3 (J_{P-C} = 12 Hz, $PCH_2CH_2CH_2$), 28.5 (J_{P-C} = 12 Hz, $PCH_2CH_2CH_2$), 30.5 (CH_2), 31.1 (CH_2), 31.9 (CH_2), 34.3 (CH_2), 50.9 (NCH_2), 51.5 (NCH_2), 122.6 (imidazol), 123.6 (imidazol), 128.8 (J_{P-C} = 7 Hz, PPh), 130.2 (J_{P-C} = 9 Hz, PPh), 131.9 (PPh), 132.5 (J_{P-C} = 12 Hz, PPh), 137.3 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −13.8, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **7c** ($C_{28}H_{40}F_6N_2P_2$): C, 57.93; H, 6.94; N, 4.83. Found: C, 57.91; H, 6.92; N, 4.84. Yield: 82%.

2.3.9. 1-(2-Diphenylphosphinoethyl)-3-octylimidazolium tetrafluoroborate (**8c**)

^1H NMR (DMSO-d_6) δ (ppm): 0.79 (t, J = 8 Hz, 3H, CH_3), 1.21–1.89 (m, 12H, CH_2), 2.69 (t, J = 12 Hz, 2H, CH_2P), 4.21 (m, 2H, NCH_2), 4.83 (m, 2H, NCH_2), 7.35–7.48 (m, 10H, Ph), 7.84 (brs, 1H, imidazol), 8.11 (brs, 1H, imidazol), 9.57 (s, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.3 (CH_3), 22.1 (CH_2), 26.5 (CH_2), 28.7 (CH_2), 28.9 (J_{P-C} = 8 Hz, PCH_2), 30.1 (CH_2), 31.6 (CH_2), 31.9 (CH_2), 50.1 (J_{P-C} = 20 Hz, NCH_2), 51.7 (NCH_2), 123.3 (imidazol), 123.8 (imidazol), 129.9 (J_{P-C} = 7 Hz, PPh), 130.9 (J_{P-C} = 9 Hz, PPh), 131.5 (PPh), 132.9 (J_{P-C} = 12 Hz, PPh), 138.6 (imidazol). ^{31}P NMR (DMSO-d_6) δ (ppm): −21.8. Anal. Calc. for **8c** ($C_{25}H_{34}F_4N_2PB$): C, 62.51; H, 7.13; N, 5.83. Found: C, 62.49; H, 7.11; N, 5.80. Yield: 77%.

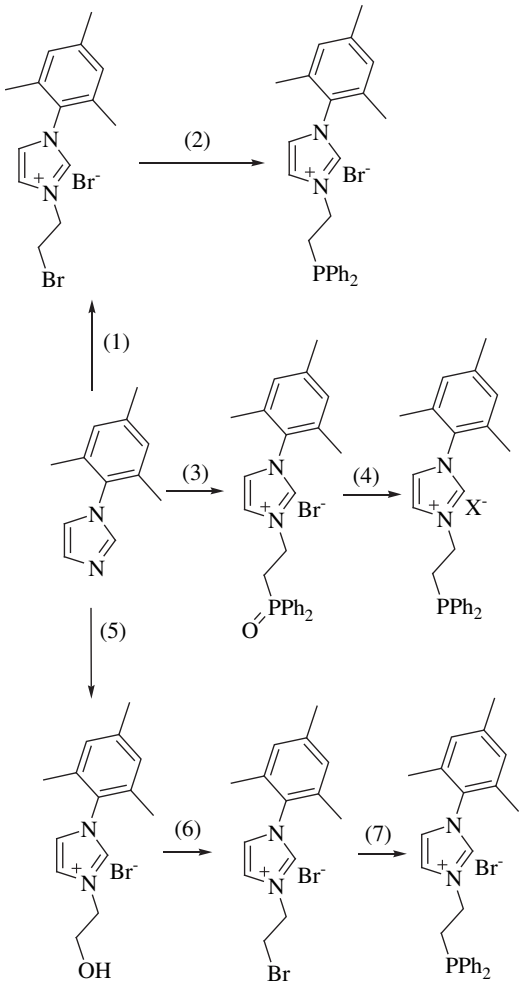
All of the prepared compounds showed spectroscopic data (^1H, ^{13}C and ^{31}P NMR) in accordance with the proposed structures.

2.4. Hydrosilylation of alkenes with triethoxysilane

Typical hydrosilylation reaction procedures were as follows: The requisite amounts of $RhCl_3$ catalyst, the phosphine functionalized with an ionic liquid, and the ionic liquid were added to a 10 mL round-bottomed flask equipped with a magnetic stirrer, and the mixture was stirred at 90 °C for 30 min. The mixture was then cooled to room temperature, whereupon the alkene and silane were added. The resulting mixture was stirred for 5 h at the appropriate temperature. At the end of the reaction, the product phase was separated by decantation and the conversion of alkene and the selectivity were determined by GC. The catalytic phase was recharged with fresh alkene and silane for the next catalysis run.

3. Results and discussion

Nolan et al. [16] described the first synthetic method for the phosphine–imidazolium cation 1-(2-diphenylphosphinoethyl)-3-mesityl-imidazolium, which was obtained in only 21% overall yield. The second method, described by Tsoureas et al. [17], involved a phosphine oxide intermediate that had to be reduced under harsh conditions. A synthetic method reported by Poli et al. [18] was based on quaternization of *N*-mesitylimidazole with 1-bromoethanol to give 1-hydroxyethylene-3-mesitylimidazolium bromide (Scheme 4). Our synthetic method is based on the quaternization of *N*-alkylimidazoles with $Br(CH_2)_nCl$ (n = 2 or 3) to give 1-(*n*-chloroalkyl)-3-alkyl-



Scheme 4. Synthesis of phosphines functionalized with imidazolium salts. Reagents and condition: (1) 1,2-dibromoethane (4.4 equiv.), THF, r.t., 2 d(23 %); (2) HPPh2 (1.1 equiv.), *t*BuOK (1.05 equiv.), DMSO, r.t., 1 h (91 %); (3)Ph2P(=O)(CH2)2Br, 150–160 °C, 4–5 d (83 %); (4) $HSiCl_3$, chlorobenzene, 120 °C, 3 h(75 %); (5) 1-bromoethanol, toluene, 120 °C, 18 h (91 %); (6) PBr_3, CH_2Cl_2, 0 °C, 15 h (78 %); (7) $HPPh_2$ (1.1 equiv.), *t*BuOK (1.05 equiv.), DMSO, r.t., 1 h (95%).

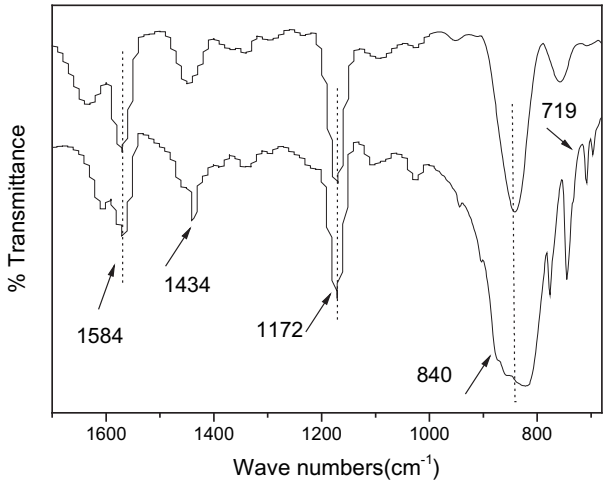
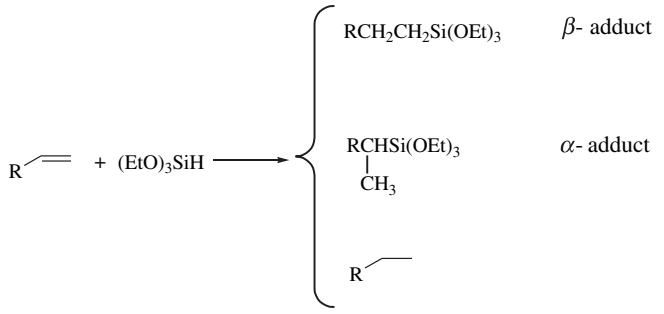


Fig. 1. IR spectra (680–1700 cm^{-1}) of **1b** and **1c**.



R= Ph, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_9H_{19}

Scheme 5. Hydrosilylation of olefins with triethoxysilane.

imidazolium salts, followed by nucleophilic substitution with $LiPPh_2$ to produce the desired ligands. A series of phosphine ligands functionalized with imidazolium salts (**1c**–**8c**) was synthesized and characterized [16–18]. Infrared spectroscopy is a useful tool for confirming the proposed chemical modifications. A band appearing in the diffuse reflection infrared Fourier-transform spectra of **1b** and **1c** at 1584 cm^{-1} can be assigned to ring-stretching of the imidazolium cation (Fig. 1). Two bands appearing in the diffuse reflection infrared Fourier-transform spectrum of **1c** at 1434 and 719 cm^{-1} may be assigned to P–Ph and Ph stretching modes, respectively (Fig. 1). All of the prepared compounds showed spectroscopic data (^1H, ^{13}C and ^{31}P NMR) in accordance with the proposed structures. Elemental analysis data and theoretical values for the 1-(*n*-chloroalkyl)-3-alkylimidazolium hexafluorophosphates (**1b**–**8b**) and phosphine–imidazolium salts (**1c**–**8c**) were in close agreement (Scheme 5).

By using these phosphine ligands functionalized with imidazolium salts, rhodium-catalyzed hydrosilylations of styrene with silanes in ionic liquids were tested. The results listed in Table 1 indicate that Wilkinson's catalyst $RhCl(PPh_3)_3$ in $BMimPF_6$ (1-methyl-3-butylimidazolium hexafluorophosphate) displayed low catalytic activity and selectivity (Table 1, entry 1). When $RhCl_3$ was mixed with the synthesized phosphine ligands functionalized with imidazolium salts (**1c**–**7c**) in $BMimPF_6$, higher catalytic activity and selectivity in favor of the β-adduct were seen. With increasing length of the alkyl chain attached to the imidazolium cation, higher catalytic activities of the complex of $RhCl_3$-phosphines functionalized with imidazolium salt were achieved, while the β/α ratio increased (Table 1, entries 2–3, 5–6). However, the catalytic activities and the β/α ratio of the $RhCl_3$-phosphines functionalized with imidazolium salts/$BMimPF_6$ catalyst systems decreased with increasing length of the alkyl chain between the imidazolium ring and the diphenylphosphine group (Table 1, entries 6–9). Phosphines bearing imidazolium moieties may function as ambivalent *P, C*-donor systems, with the electron-rich imidazolium moiety providing a suitable modification that stabilizes the Rh-phosphine, which may be due to formation of Rh-*N*-heterocyclic carbine (NHC) complex during the catalytic process [19,20]. Although the rhodium complexe employing phosphines with 2-imidazolium as ligands (**d**) resulted in the higher chemoselectivity for the β-adduct than that of present catalyst system ($RhCl_3$-**2c**), the conversion was excellent in the presence of the simple catalyst system derived from $RhCl_3$ and phosphine ligands functionalized with imidazolium salts (**2c**). Based on the screening of phosphine ligands, it was concluded that the best catalytic activity and selectivity in favor of the β-adduct were obtained when 1-(2-diphenylphosphinoethyl)-3-octylimidazolium hexafluorophosphate (**4c**) was used as the ligand.

It is well known that the nature of the anion has a strong impact on the physicochemical properties of imidazolium based ionic liquid, which could result in pronounced effect between the rhodium complexes and the reactants. In this case, it was observed that nucleophilic BF_4^- anion could reduce the solubility of the silane in the hydrophilic ionic liquid $BMimBF_4$. Therefore, low catalytic activity was observed when the hydrosilylation reaction of styrene with triethoxysilane was conducted in $BMimBF_4$ in the presence **8c**, and the conversion of styrene was just 64.2%. And this phenomenon is consistent with the former report [15].

When other alkenes, such as 1-hexene, 1-octene, or 4-chlorostyrene, were used in place of styrene as the substrate, excellent conversions and selectivities were obtained with the $RhCl_3$-**4c**/$BMimPF_6$ catalyst system (Table 1, entries 11–13).

Catalyst systems of $RhCl_3$ with phosphine–imidazolium salts (**1c**–**7c**) as ligands show a pronounced solubility in $BMimPF_6$. For ease of reuse of the catalysts, they were specially designed to be used in ionic liquid biphasic systems. It was verified that $RhCl_3$ with

Table 1
Hydrosilylation reactions of styrene with triethoxysilane.

Entry	Catalyst (% substrate mol)	Ligand	Substrate	Conversion %	Selectivity %			β/α
					β	α	Ethylbenzene	
1	$Rh(PPh_3)_3Cl$ 0.1	–	Styrene	81.9	80.9	15.9	3.2	5.1
2	$RhCl_3$ 0.02	**1c**	Styrene	96.2	84.7	13.2	2.1	6.4
3	$RhCl_3$ 0.02	**2c**	Styrene	97.5	91.1	6.8	2.1	13.4
4[a]	**d**		Styrene	95.7	96.6	1.9	1.5	50.8
5	$RhCl_3$ 0.02	**3c**	Styrene	98.8	92.2	5.7	2.1	16.2
6	$RhCl_3$ 0.02	**4c**	Styrene	99.9	94.3	3.5	2.2	26.9
7	$RhCl_3$ 0.02	**5c**	Styrene	98.1	90.6	2.5	6.9	36.2
8	$RhCl_3$ 0.02	**6c**	Styrene	95.3	82.7	2.1	15.2	39.4
9	$RhCl_3$ 0.02	**7c**	Styrene	94.2	78.0	2.1	19.9	37.1
10	$RhCl_3$ 0.02	**8c**	Styrene	64.2	93.9	3.6	2.5	26.1
11	$RhCl_3$ 0.02	**4c**	4-Chloro-styrene	100	95.6	2.8	1.6	34.1
12	$RhCl_3$ 0.01	**4c**	1-Hexene	100	97.5	–	2.5	–
13	$RhCl_3$ 0.01	**4c**	1-Octene	100	97.4	–	2.6	–
14[b]	$RhCl_3$ 0.02	**4c**	Styrene	98.9	94.1	3.5	2.4	26.9
15[c]	$RhCl_3$ 0.02	**4c**	Styrene	97.6	94.2	3.5	2.3	26.9
16[d]	$RhCl_3$ 0.02	**4c**	Styrene	95.4	94.0	3.4	2.6	27.6

Reaction conditions: styrene 2.5 mmol; triethoxysilane 3.0 mmol; 90 °C, 2 h; ligand/$RhCl_3$: 1:5; $BMimPF_6$: 0.5 mL.
[a] 70 °C, 5 h; Catalyst **d**: Tri[1-ethyl-2-diphenylphosphino-3-butylimidazolium hexafluorophosphate] rhodium chloride [13].
[b] Second run.
[c] Third run.
[d] Fourth run.

4c as ligand in $BMimPF_6$ could be reused without significant loss of catalytic activity or selectivity (Table 1, entries 14–16).

4. Conclusion

A series of phosphine ligands functionalized with imidazolium salts has been synthesized and characterized. These phosphines functionalized with imidazolium salts (**1c**–**7c**) have been tested as ligands for the rhodium-catalyzed hydrosilylation of alkenes in $BMimPF_6$, and higher catalytic activity and selectivity in favor of the β-adduct were observed. Phosphines bearing imidazolium moieties may function as ambivalent *P*, *C*-donor systems, with the electron-rich imidazolium moiety providing a suitable modification that stabilizes the Rh-phosphine, which may be due to formation of Rh-NHC complex during the catalytic process. The best catalytic activity and selectivity in favor of the β-adduct were obtained when **4c** was used as the ligand. Furthermore, the $RhCl_3$-**4c**/$BMimPF_6$ catalyst system could be reused without noticeable loss of catalytic activity or selectivity.

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