Journal of Organometallic Chemistry 695 (2010) 431–436

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Phosphines with 2-imidazolium ligands enhance the catalytic activity and selectivity of rhodium complexes for hydrosilylation reactions

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ARTICLE INFO

Article history:
Received 31 August 2009
Received in revised form 19 October 2009
Accepted 23 October 2009
Available online 27 October 2009

Keywords:
Rhodium complex
Hydrosilylation
2-Imidazolium phosphine ligand

ABSTRACT

Phosphines with 2-imidazolium ligands can specifically vary their physical and chemical properties by altering the attached substituents. Rhodium complexes (**1b**–**7b**) exhibited excellent catalytic activity and selectivity for hydrosilylation of olefins. The selectivity of the β-adduct clearly increased when the length of the alkyl chain bound to the imidazolium cation increased. Rhodium complex **1b** in $BMimPF_6$ can be reused without noticeable loss of catalytic activity and selectivity.

1. Introduction

Hydrosilylation is one of the most important Si–C bond formation reactions within organosilicon chemistry. Many organosilicon monomers containing functional groups have been synthesized via this reaction [1]. Transition metal complexes, such as tertiary phosphine complexes of rhodium, palladium, platinum and nickel have been applied as homogeneous catalysts for hydrosilylation reactions due to the stereo-, regio- and/or enantioselectivity of this reaction [2,3]. In view of homogeneously catalytic processes, apart from the metal center used, these ligands also play an important role in the reaction. Phosphines bearing 2-imidazolyl moieties are interesting ligands and may function as ambivalent P, N-donor systems which are capable of binding both soft and hard transition metals [4–8].

Dialkylimidazolium salts can also specifically alter their physical and chemical properties by changing the attached substituents and associated anions [9,10]. It is therefore to be expected that phosphines bearing 2-imidazolium ligands should exhibit different effects on reaction processes. Furthermore, because of the heterocyclic groups, these ligands are expected to enhance the solubility of metal complexes in ionic liquids.

The synthesis of a series of 2-imidazolium phosphines and their application in hydrosilylation is reported here. The activity and selectivity influenced by rhodium complexes employing 2-imidazolium phosphines as ligands in ionic liquid are investigated in the hydrosilylation of olefins with triethoxysilane (Scheme 1). Phosphines with 2-imidazolium ligands can specifically vary their physical and chemical properties by altering the attached substituents of the imidazolium cation and it is therefore expected that different reaction performances will be exhibited by using this kind of novel catalyst (see Schemes 2 and 3).

2. Experimental

2.1. General methods

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.

$R_1R_2imPF_6$ (R_1: CH_3, R_2: C_2H_5; R_1: CH_3, R_2: C_4H_9; R_1: CH_3, R_2: C_6H_{11}; R_1: C_2H_5, R_2: C_4H_9; R_1: C_4H_9, R_2: C_4H_9; R_1: C_4H_9, R_2: C_6H_{11}; R_1: C_4H_9, R_2: C_8H_{17}) and 1-methyl-3-butylimidazolium tetrafluoroborate ($BMimBF_4$) were, respectively, prepared according to literature procedures [11].

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).

^1H, ^{13}C and ^{31}P NMR spectra were measured using a Bruker AV400 MHz spectrometer operating at 400.13, 100.62 and 161.97 MHz, respectively. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to residual proton of $CDCl_3$ (^1H: δ

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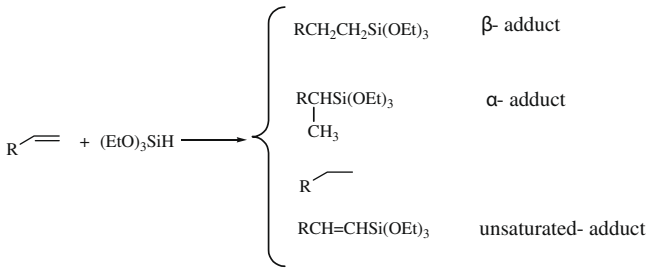
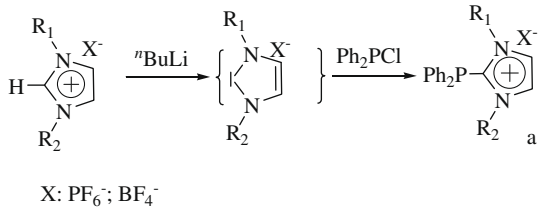
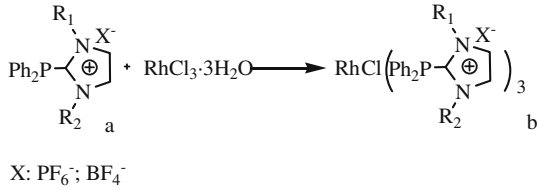
doi:10.1016/j.jorganchem.2009.10.029



Scheme 1. Hydrosilylation of olefins with triethoxysilane.



Scheme 2. Preparation of 2-imidazolium phosphines.



Scheme 3. Preparation of rhodium complexes employing the 2-imidazolium phosphines as ligands.

7.24; ^{13}C δ 77.0) and DMSO-d_6 (^{1}H: δ 2.50; ^{13}C δ 39.5). ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 external standard.

2.2. Preparation of 2-imidazolium phosphines

To a solution of $R_1R_2imPF_6$ (3.0 mmol) dissolved in CH_2Cl_2 (20 mL) (dried over P_4O_{10}), was added ^{n}BuLi (3.0 mmol, 15% in *n*-hexane) at −78 °C, within a period of 15 min. After stirring for 45 min, the reaction mixture was charged, within 20 min, with Ph_2PCl (3.0 mmol) at −78 °C. The reaction mixture was warmed up gradually to room temperature over night. Thereafter the solution was extracted with three aliquots of deaerated water (10 mL). The organic phase was dried over Na_2SO_4. After evaporation of the solvent in vacuo the cream-colored solid obtained was dried. The spectroscopic data (^{1}H NMR, ^{13}C NMR and ^{31}P NMR) of the prepared compounds were in agreement with the assigned structures.

1-Methyl-2-diphenylphosphino-3-ethylimidazolium hexafluorophosphate (**1a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.84 (t, J = 8 Hz, 3H, CH_3), 3.86 (m, 3H, CH_3), 4.67 (m, 2H, CH_2), 7.51–7.76 (m, 10H, Ph), 7.72 (brs, 1H, imidazol), 8.24 (brs, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 15.9, 37.9 (J = 7 Hz), 45.6 (J = 10 Hz), 125.6, 128.3, 129.0 (J = 6 Hz), 130.3 (J = 7 Hz), 131.6, 132.9 (J = 13 Hz), 142.1 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −23.8, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **1a**: C, 49.10; H, 4.58; N, 6.36. Found: C, 49.21; H, 4.56; N, 6.33%.

1-Methyl-2-diphenylphosphino-3-butylimidazolium hexafluorophosphate (**2a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.86 (t, J = 8 Hz, 3H, CH_3), 1.38 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 3.56 (m, 3H, CH_3), 4.18 (m, 2H, CH_2), 7.38–7.57 (m, 10H, Ph), 7.74 (brs, 1H, imidazol), 8.57 (brs, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.6, 19.1, 32.4, 37.8 (J = 7 Hz), 50.0 (J = 11 Hz), 126.0, 128.2, 128.5 (J = 6 Hz), 130.2 (J = 9 Hz), 130.8, 133.1 (J = 14 Hz), 142.3 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −25.5, −143.1 (PF_6^-, J_{PF} = 705.2 Hz). Anal. Calc. for **2a**: C, 51.29; H, 5.16; N, 5.98. Found: C, 51.13; H, 5.17; N, 5.97%.

1-Methyl-2-diphenylphosphino-3-hexylimidazolium hexafluorophosphate (**3a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.86 (t, J = 8 Hz, 3H, CH_3), 1.36–1.60 (m, 8H, CH_2), 3.58 (m, 3H, CH_3), 4.18 (m, 2H, CH_2), 7.38–7.58 (m, 10H, Ph), 7.74 (brs, 1H, imidazol), 8.60 (brs, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.1, 22.3, 29.8, 30.4, 31.0, 37.8 (J = 7 Hz), 50.2 (J = 11 Hz), 126.0, 128.3, 128.6 (J = 6 Hz), 130.3 (J = 9 Hz), 130.8, 133.0 (J = 14 Hz), 142.3 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −30.0, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **3a**: C, 53.23; H, 5.69; N, 5.64. Found: C, 53.02; H, 5.71; N, 5.65%.

1-Ethyl-2-diphenylphosphino-3-butylimidazolium hexafluorophosphate (**4a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.84 (t, J = 8 Hz, 3H, CH_3), 0.87 (t, J = 8 Hz, 3H, CH_3), 1.34–1.61 (m, 4H, CH_2), 4.18–4.65 (m, 4H, CH_2), 7.38–7.58 (m, 10H, Ph), 7.74 (brs, 1H, imidazol), 8.59 (brs, 1H, imidazol).^{13}C NMR (DMSO-d_6) δ (ppm): 13.6, 14.1, 19.1, 32.2, 45.8 (J = 10 Hz), 50.2 (J = 11 Hz), 126.0, 128.1, 128.4 (J = 6 Hz), 130.4 (J = 7 Hz), 131.0, 132.7 (J = 12 Hz), 142.3 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −27.5, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **4a**: C, 52.29; H, 5.43; N, 5.81. Found: C, 52.28; H, 5.44; N, 5.83%.

1,3-Butyl-2-diphenylphosphino-imidazolium hexafluorophosphate (***5a***): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.89 (t, J = 8 Hz, 6H, CH_3), 1.31–1.89 (m, 8H, CH_2), 4.24 (m, 4H, CH_2), 7.44–7.63 (m, 10H, Ph), 8.20 (s, 2H, imidazol).^{13}C NMR (DMSO-d_6) δ (ppm): 13.8, 19.1, 31.7, 50.2 (J = 11 Hz), 126.0, 130.2 (J = 6 Hz), 131.3 (J = 8 Hz), 132.6, 133.0 (J = 12 Hz), 142.2 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −28.5, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **5a**: C, 54.12; H, 5.92; N, 5.49. Found: C, 54.13; H, 5.94; N, 5.51%.

1-Butyl-2-diphenylphosphino-3-hexylimidazolium hexafluorophosphate (**6a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.86 (t, J = 8 Hz, 3H, CH_3), 0.92 (t, J = 8 Hz, 3H, CH_3), 1.30–1.90 (m, 12H, CH_2), 4.20–4.26 (m, 4H, CH_2), 7.46–7.62 (m, 10H, Ph), 7.79 (brs, 1H, imidazol), 8.24 (brs, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7, 14.1, 19.1, 22.5, 25.7, 30.6, 31.3, 32.4, 50.2 (J = 11 Hz), 50.3 (J = 11 Hz), 126.2, 128.4, 129.4 (J = 7 Hz), 130.5 (J = 9 Hz), 131.3, 133.4 (J = 12 Hz), 142.2 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −31.4, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **6a**: C, 55.76; H, 6.36; N, 5.20. Found: C, 55.75; H, 6.37; N, 5.19%.

1-Butyl-2-diphenylphosphino-3-octylimidazolium hexafluorophosphate (**7a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.83 (t, J = 8 Hz, 3H, CH_3), 0.94 (t, J = 8 Hz, 3H, CH_3), 1.31–1.92 (m, 16H, CH_2), 4.20–4.25 (m, 4H, CH_2), 7.40–7.58 (m, 10H, Ph), 7.78 (brs, 1H, imidazol), 8.74 (brs, 1H, imidazol).^{13}C NMR (DMSO-d_6) δ (ppm): 13.6, 14.2, 19.1, 22.7, 25.8, 28.8, 30.1, 31.5, 31.6, 32.2, 50.1 (J = 11 Hz), 50.3 (J = 11 Hz), 125.0, 126.5, 128.9 (J = 7 Hz), 130.3 (J = 9 Hz), 131.0, 132.8 (J = 12 Hz), 142.0 (J = 50 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −34.4, −143.1 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **7a**: C, 57.24; H, 6.76; N, 4.94. Found: C, 57.23; H, 6.79; N, 4.94%.

To a solution of $BMimBF_4$ (3.0 mmol) dissolved in CH_2Cl_2 (20 mL) (dried over P_4O_{10}), was added ^{n}BuLi (3.0 mmol, 15% in *n*-hexane) at −78 °C, within a period of 15 min. After stirring for 45 min, the reaction mixture was charged, within 20 min, with Ph_2PCl (3.0 mmol) at −78 °C. The reaction mixture was warmed up gradually to room temperature over night. Thereafter the solution was extracted with three aliquots of deaerated water (10 ml). The organic phase was dried over Na_2SO_4. After evaporation of the solvent in vacuo the cream-colored solid obtained was dried. The

spectroscopic data (^{1}H NMR, ^{13}C NMR and ^{31}P NMR) of the prepared compounds were in agreement with the assigned structures.

1-Methyl-2-diphenylphosphino-3-butylimidazolium tetrafluoroborate (**8a**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.76 (t, J = 8 Hz, 3H, CH_3), 1.16 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 3.63 (m, 3H, CH_3), 4.38 (m, 2H, CH_2), 7.31–7.47 (m, 10H, Ph), 8.40 (brs, 1H, imidazol), 8.90 (brs, 1H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.3, 19.5, 33.1, 38.7 (J = 5 Hz), 50.4 (J = 12 Hz), 126.2, 128.4(J = 6 Hz), 128.8, 130.2 (J = 9 Hz), 130.9, 132.6 (J = 18 Hz), 142.2 (J = 52 Hz). ^{31}P NMR (DMSO-d_6) δ (ppm): −26.7. Anal. Calc. for **8a**: C, 58.57; H, 5.86; N, 6.83. Found: C, 58.56; H, 5.90; N, 6.83%.

2.3. Preparation of rhodium complexes employing the 2-imidazolium phosphines as ligands

A solution of 2-imidazolium phosphine (a) (2.5 mmol) in CH_3OH (10 mL) was treated with $RhCl_3{\cdot}3H_2O$ (0.5 mmol). The mixture was stirred at 70 °C for 3 h. After filtration, the solid was washed with diethyl ether, purified by silica gel column chromatography and then dried *in vacuo*. All the prepared compounds showed spectroscopic data (^{1}H NMR, ^{13}C NMR and ^{31}P NMR) in accordance with the assigned structures.

Tri[1-methyl-2-(diphenylphosphino)-3-ethylimidazolium hexafluorophosphate] rhodium chloride (**1b**)**:** ^{1}H NMR (DMSO-d_6) δ (ppm): 0.84 (t, J = 8 Hz, 9H, CH_3), 3.84 (m, 9H, CH_3), 4.65 (m, 6H, CH_2), 7.51–7.76 (m, 30H, Ph), 7.72 (br, 3H, imidazol), 8.29 (br, 3H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 14.2, 37.1 (J = 7 Hz), 44.6 (J = 6 Hz), 125.6, 127.9, 128.9, 130.2, 131.1, 134.3, 141.8, due to overlapping of signals, the carbon resonances from δ 125 to 135 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −18.8 (J_{PRh} = 161 Hz), −143.0 (PF_6^-, J_{PF} = 707 Hz). Anal. Calc. for **1b**: C, 44.42; H, 4.11; N, 5.76. Found: C, 44.53; H, 4.14; N, 5.79%.

Tri[1-methyl-2-diphenylphosphino-3-butylimidazolium hexafluorophosphate] rhodium chloride (**2b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.76 (t, J = 8 Hz, 9H, CH_3), 1.26–1.75 (m, 12H, CH_2), 3.55 (m, 9H, CH_3), 4.18 (m, 6H, CH_2), 7.38–7.70 (m, 30H, Ph), 8.20 (brs, 3H, imidazol), 8.62 (brs, 3H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7, 19.2, 31.8, 37.9 (J = 7 Hz), 50.1 (J = 11 Hz), 125.2, 126.0, 128.3, 130.3, 131.1, 134.9, 142.3, due to overlapping of signals, the carbon resonances from δ 125 to 135 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −21.7 (J_{PRh} = 177.1 Hz), −143.0 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **2b**: C, 46.67; H, 4.67; N, 5.44. Found: C, 46.87; H, 4.69; N, 5.46%.

Tri[1-methyl-2-diphenylphosphino-3-hexylimidazolium hexafluorophosphate] rhodium chloride (**3b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.78 (t, J = 8 Hz, 9H, CH_3), 1.32–1.64 (m, 24H, CH_2), 3.57 (m, 9H, CH_3), 4.18 (m, 6H, CH_2), 7.38–7.57 (m, 30H, Ph), 7.74 (brs, 3H, imidazol), 8.61 (brs, 3H, imidazol), ^{13}C NMR (DMSO-d_6) δ (ppm): 14.2, 22.2, 28.8, 30.9, 31.2, 37.9 (J = 7 Hz), 50.3 (J = 11 Hz), 125.3, 126.1, 128.3, 130.2, 131.3, 136.5, 142.3, due to overlapping of signals, the carbon resonances from δ 125 to 137 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −27.8 (J_{PRh} = 132 Hz), −143.0 (PF_6^-, J = 706.8 Hz). Anal. Calc. for **3b**: C, 48.68; H, 5.16; N, 5.16. Found: C, 48.91; H, 5.18; N, 5.17%.

Tri[1-ethyl-2-diphenylphosphino-3-butylimidazolium hexafluorophosphate] rhodium chloride (**4b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.86 (t, J = 8 Hz, 9H, CH_3), 0.89 (t, J = 8 Hz, 9H, CH_3), 1.36–1.60 (m, 12H, CH_2), 4.18–4.64 (m, 12H, CH_2), 7.38–7.58 (m, 30H, Ph), 7.74 (brs, 3H, imidazol), 8.60 (brs, 3H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7, 14.1, 19.2, 31.8, 45.8 (J = 10 Hz), 50.1 (J = 11 Hz), 125.4, 126.2, 128.2, 129.4, 132.1, 135.2, 142.2, due to overlapping of signals, the carbon resonances from δ 125 to 136 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −23.4 (J_{PRh} = 132 Hz), −143.0 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **4b**: C, 47.70; H, 4.92; N, 5.30. Found: C, 47.89; H, 4.93; N, 5.31%.

Tri[1,3-dibutyl-2-diphenylphosphinoimidazolium hexafluorophosphate]rhodium chloride (**5b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.86 (t, J = 8 Hz, 18H, CH_3), 1.30–1.88 (m, 24H, CH_2), 4.26 (m, 12H, CH_2), 7.44–7.60 (m, 30H, Ph), 7.98 (brs, 6H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7, 19.2, 31.8, 50.1(J = 11 Hz), 126.1, 128.4, 130.3, 132.3, 133.1, 136.0, due to overlapping of signals, the carbon resonances from δ 125 to 137 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −25.7 (J_{PRh} = 132 Hz), −143.0 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **5b**: C, 49.61; H, 5.39; N, 5.03. Found: C, 49.63; H, 5.41; N, 5.03%.

Tri[1-butyl-2-diphenylphosphino-3-hexylimidazolium hexafluorophosphate] rhodium chloride (**6b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.78 (t, J = 8 Hz, 9H, CH_3), 0.89 (t, J = 8 Hz, 9H, CH_3), 1.31–1.88 (m, 36H, CH_2), 4.18–4.23 (m, 12H, CH_2), 7.46–7.61 (m, 30H, Ph), 7.77 (brs, 3H, imidazol), 8.72 (brs, 3H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7, 14.3, 19.2, 22.8, 25.9, 30.9, 31.5, 32.1, 50.1 (J = 11 Hz), 50.3 (J = 11 Hz), 125.7, 127.7, 128.5, 131.0, 132.8, 134.7, 142.2, due to overlapping of signals, the carbon resonances from δ 125 to 137 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −28.9 (J_{PRh} = 148.1 Hz), −143.0 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **6b**: C, 51.34; H, 5.82; N, 4.79. Found: C, 51.47; H, 5.85; N, 4.81%.

Tri[1-butyl-2-diphenylphosphino-3-octylimidazolium hexafluorophosphate] rhodium chloride (**7b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.67–0.82 (m, 18H, CH_3), 1.31–1.52 (m, 48H, CH_2), 3.34–4.13 (m, 12H, CH_2), 7.38–7.48 (m, 30H, Ph), 7.78 (brs, 3H, imidazol), 8.20 (brs, 3H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.7, 14.4, 19.3, 22.5, 25.9, 28.8, 30.2, 31.6, 31.7, 32.2, 50.1 (J = 11 Hz), 50.3 (J = 11 Hz), 123.0, 126.8, 128.6, 130.3, 131.0, 132.9, 141.9, due to overlapping of signals, the carbon resonances from δ 125 to 133 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −30.5 (J_{PRh} = 132 Hz), −143.0 (PF_6^-, J_{PF} = 706.8 Hz). Anal. Calc. for **7b**: C, 52.92; H, 6.21; N, 4.57. Found: C, 53.17; H, 6.24; N, 4.59%.

Tri[1-methyl-2-diphenylphosphino-3-butylimidazolium tetrafluoroborate] rhodium chloride (**8b**): ^{1}H NMR (DMSO-d_6) δ (ppm): 0.83 (t, J = 8 Hz, 9H, CH_3), 1.10–1.79 (m, 12H, CH_2), 3.51 (m, 9H, CH_3), 3.84 (m, 6H, CH_2), 7.33–7.69 (m, 30H, Ph), 8.69 (brs, 3H, imidazol), 8.82 (brs, 3H, imidazol). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.1, 19.2, 32.2, 37.8 (J = 6 Hz), 50.4 (J = 12 Hz), 125.2, 127.5, 128.1, 130.3, 131.3, 132.9, 142.1, due to overlapping of signals, the carbon resonances from δ 125 to 135 were listed without identification of the ^{31}P splitting. ^{31}P NMR (DMSO-d_6) δ (ppm): −22.6 (J_{PRh} = 161 Hz). Anal. Calc. for **8b**: C, 52.64; H, 5.30; N, 6.14. Found: C, 52.61; H, 5.26; N, 6.13%.

2.4. Hydrosilylation of alkene with triethoxysilane

Typical hydrosilylation reaction procedures were as follows: a given amount of catalyst and ionic liquid were added to a 10 mL round bottomed flask equipped with a magnetic stirrer and the alkene and silane were then 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. The catalyst was recharged with fresh alkene and silane for the next catalytic run.

2.4.1. Hydrosilylation of styrene with triethoxyslane

β-Adduct [triethoxy(phenethyl)silane]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.00 (t, J = 8 Hz, 2H, Si–CH_2), 1.24 (t, J = 9 Hz, 9H, CH_3), 2.74 (t, J = 8 Hz, 2H, CH_2), 3.84 (q, J = 8 Hz, 6H, O–CH_2), 7.16–7.27 (m, 5H, Ph).

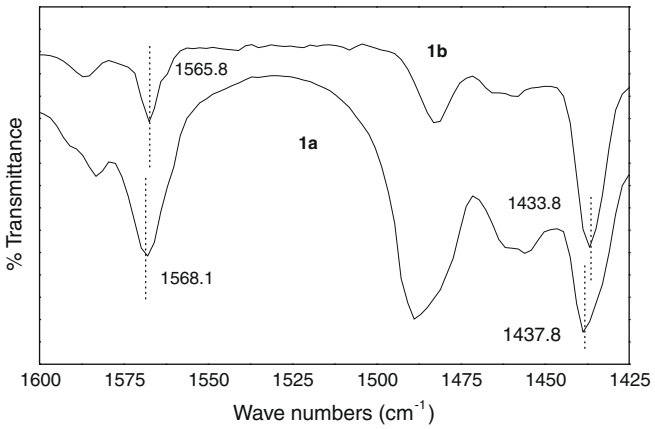


Fig. 1. IR spectra (1415–1600 cm^{-1}) of **1a** and **1b**.

α-Adduct [triethoxy(1-phenylethyl)silane]: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.18 (t, *J* = 8 Hz, 9H, CH_3), 1.33 (d, *J* = 8 Hz, 3H, CH_3), 3.65 (q, *J* = 8 Hz, 1H, Si–CH), 3.76 (q, *J* = 8 Hz, 6H, O–CH_2), 7.12-7.19 (m, 5H, Ph).

Ethylbenzene: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.15 (t, *J* = 8 Hz, 3H, CH_3), 2.64 (q, *J* = 8 Hz, 2H, CH_2), 7.11–7.25 (m, 5H, Ph).

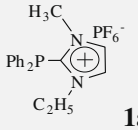
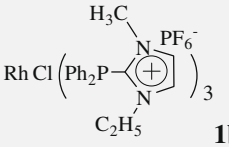
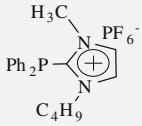
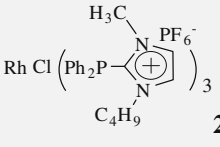
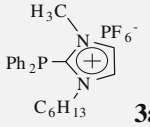
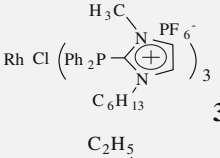
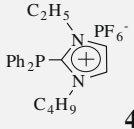
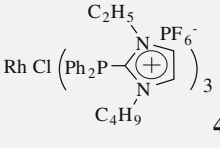
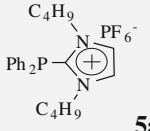
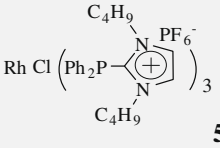
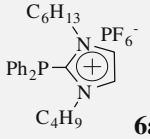
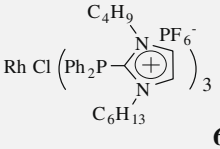
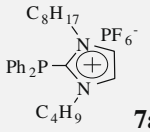
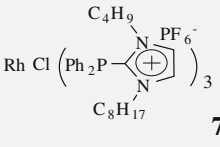
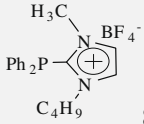
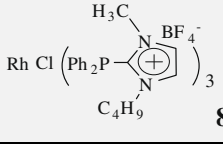
2.4.2. Hydrosilylation of 1-hexene with triethoxyslane

β-Adduct (hexyltriethoxysilane): ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.64 (t, *J* = 6 Hz, 2H, Si–CH_2), 0.89 (t, *J* = 8 Hz, 3H, CH_3), 1.22–1.42 (m, 17H, CH_2 CH_3), 3.81 (q, *J* = 8 Hz, 6H, O–CH_2).

3. Results and discussion

Infrared spectroscopy is a useful tool to confirm the chemical modifications proposed. Two bands present in the diffuse reflection infrared Fourier-transform spectra of **1a** at 1568.1 cm^{-1} and

Table 1
Preparation of 2-imidazolium phosphines and rhodium complexes employing the 2-imidazolium phosphines as ligands.

Entry	Product a	Yield[a] (%)	Product b	Yield[a] (%)
1	 **1a**	90	 **1b**	92
2	 **2a**	88	 **2b**	88
3	 **3a**	88	 **3b**	90
4	 **4a**	86	 **4b**	90
5	 **5a**	85	 **5b**	87
6	 **6a**	81	 **6b**	83
7	 **7a**	83	 **7b**	77
8	 **8a**	87	 **8b**	92

[a] Isolated yields.

Table 2
Effect of b on the hydrosilylation reaction.

Entry	Catalyst (% substrate mol)	Substrate	Conversion (%)	Selectivity (%)				TON
				β	α	Alkane	Un-saturated	
1	$RhCl(PPh_3)_3$ 0.1	Styrene	78.1	81.2	16.5	2.3	–	781
2	**1b** 0.1	Styrene	100	90.0	4.1	5.9	–	1000
3	**1b** 0.05	Styrene	100	90.1	4.1	5.8	–	2000
4	**1b** 0.01	Styrene	88.7	89.3	4.2	6.5	–	8870
5	**1b** 0.02	Styrene	100	89.8	4.1	6.1	–	5000
6	**2b** 0.02	Styrene	99.4	91.6	3.1	5.3	–	4970
7	**3b** 0.02	Styrene	96.1	94.9	1.6	3.5	–	4805
8	**4b** 0.02	Styrene	95.7	96.6	1.9	1.5	–	4785
9	**5b** 0.02	Styrene	94.5	97.3	1.2	1.5	–	4725
10	**6b** 0.02	Styrene	92.1	99.4	–	0.6	–	4605
11	**7b** 0.02	Styrene	90.4	97.7	–	2.3	–	4520
12[a]	**8b** 0.02	Styrene	66.7	90.8	3.4	5.8	–	3335
13	**1b** 0.005	1-Hexene	100	99.1	–	0.9	–	20,000
14	**1b** 0.005	1-Heptene	100	98.7	–	1.3	–	20,000
15	**1b** 0.005	1-Octene	100	99.0	–	1.0	–	20,000
16	**1b** 0.005	1-Undene	100	98.8	–	1.2	–	20,000
17[b]	**1b** 0.02	Styrene	98.7	89.9	4.1	6.0	–	4935
18[c]	**1b** 0.02	Styrene	98.8	89.8	4.1	6.1	–	4940
19[d]	**1b** 0.02	Styrene	98.5	89.8	4.0	6.2	–	4925

Reaction conditions: alkene 2.5 mmol, triethoxysilane 3.0 mmol, 70 °C, 5 h, $BMimPF_6$ 0.5 mL.
[a] $BMimBF_4$ 0.5 mL.
[b] Second run.
[c] Third run.
[d] Fourth run.

1b at 1565.8 cm^{-1}, are assigned to the presence of imidazolium cation cycle coupling [12] (Fig. 1). The band presents in the diffuse reflection infrared Fourier-transform spectra of **1a** at 1437.8 cm^{-1}, is assigned to the presence of P–Ph stretching [13]. The spectrum also shows the band for **1b** presents at 1433.8 cm^{-1} (Fig. 1). Introduction of Rh into **1a** causes a low-field shift in the infrared spectrum demonstrating that Rh is linked to **1a**. Moreover, in the ^{31}P NMR spectra the 2-imidazolium phosphines (**1a**–**7a**) shows singlets (−21.8 to −34.4 ppm) in a shift range typical for tertiary arylalkyl phosphines bearing C-bound heterocyclic substituents. ^{31}P chemical shifts at high frequency occur with an increasing alkyl chain length and ^{31}P chemical shifts at low frequency occur when Rh links to the ligands. Elemental analysis data and theoretical values for 2-imidazolium phosphines (**1a**–**8a**) and rhodium complexes employing the 2-imidazolium phosphines as ligands (**1b**–**8b**) are in close agreement. (Table 1)

Wilkinson's catalyst $RhCl(PPh_3)_3$ in $BMimPF_6$ (1-methyl-3-butylimidazolium hexafluorophosphate) has low catalytic activity and selectivity (Table 2, entry 1). However, Rh complexes employing 2-imidazolium phosphines as ligands (**1b**–**7b**) exhibit greater catalytic activity and selectivity. The electron-rich heterocycle provides a suitable framework that stabilizes the Rh-phosphine center located between the two nitrogen atoms. It is possible that close proximity of the positive charge to the phosphorus atom greatly enhances the catalytic activity, affording highly efficient catalytic activity and stable metal centers. Although the catalytic activities of Rh complexes employing the 2-imidazolium phosphines as ligands (**1b**–**7b**), slightly decreased with increasing length of alkyl chain, the selectivity of the β-adduct clearly increased and no α-adduct can be detected at all when **6b** and **7b** are used as catalysts. This demonstrates that the attached substituents on the nitrogen atoms have a significant impact on Rh complexes as catalysts and that fine tuning the steric and electronic properties of the substituents on the nitrogen atoms affords different catalytic activity. It is possible that the Rh complexes employing the 2-imidazolium phosphines as ligands (**1b**–**7b**) can stabilize the intermediate states. The different substituents on the nitrogen atoms result in different steric hindrances of the catalytic center and different electronic properties. The effect of the steric hindrances may be more than the effect of electronic properties and so the selectivity of the β-adduct increased with increasing length of alkyl chain.

From Table 2 (entries 2–5) it is shown that the conversion of styrene increases with increasing amounts of **1b** used; the selectivity remains constant.

Hydrosilylation reaction of styrene with triethoxysilane was conducted in $BMimBF_4$ in the presence **8b**. However, **8b** in $BMimBF_4$ shows low catalytic activity, and the conversion of styrene is 66.7%. Therefore, we can conjecture that the counter ions had some impact on the hydrosilylation reaction. The counter ion BF_4^- is more nucleophilic than PF_6^-, and it reduced the solubility of silane in the hydrophilic ionic liquid $BMimBF_4$.

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 the **1b** catalyst.

Rhodium complexes employing the 2-imidazolium phosphines as ligands (**1b**–**7b**) show a pronounced solubility in $BMimPF_6$. They are specially designed to be used in ionic liquid biphasic systems and have been employed to circumvent catalyst problems. **1b** in $BMimPF_6$ can be reused without noticeable loss of catalytic activity and selectivity (Table 2, entries 5, 17–19).

4. Conclusion

2-Imidazolium phosphines can specifically vary their physical and chemical properties by altering the attached substituents. Rhodium complexes employing 2-imidazolium phosphines as ligands (**1b**–**7b**) exhibited greater catalytic activity and selectivity. The electron-rich heterocycle provides a suitable framework that stabilizes the Rh-phosphine center located between the two nitrogen atoms. It is possible that close proximity of the positive charge to the phosphorus atom greatly enhances the catalytic activity and can afford highly efficient catalytic activity. The selectivity of the β-adduct clearly increased with increasing length of alkyl chain. **1b** in $BMimPF_6$ can be reused without noticeable loss of catalytic activity and selectivity.

Acknowledgment

We thank the Foundation of Zhejiang Educational Committee (20070466) for financial support.

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