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Synthesis of rhodium *N*-heterocyclic carbene complexes and their catalytic activity in the hydrosilylation of alkenes in ionic liquid medium

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ABSTRACT

Rhodium complexes bearing *N*-heterocyclic carbene (NHC) ligands were prepared from bis(η^4-1,5-cyclooctadiene) dichlorodirhodium and 1-alkyl-3-methylimidazolium-2-carboxylate, and the catalytic properties of rhodium complexes prepared in the hydrosilylation of alkenes in ionic liquid media were investigated. It was found that both the catalytic activity and selectivity of the rhodium complexes bearing NHC ligands were influenced by the attached substituents of the imidazolium cation. Additionally, rhodium complexes bearing NHC ligands in ionic liquid $BMimPF_6$ could be reused without noticeable loss of catalytic activity and selectivity.

1. Introduction

Transition metal complexes with *N*-heterocyclic carbenes (NHCs) have attracted considerable interest over the last two decades [1,2]. Many transition metal complexes with NHCs have been synthesized and provided the powerful homogeneous catalysts [3,4]. The NHCs most commonly encountered are based on the imidazole ring system. This electron-rich heterocycle provides a suitable framework that stabilizes the carbene center located between two nitrogen atoms [5], and in fact behaves like typical σ-donor ligand [6]. In general, NHCs can be synthesized from a precursor imidazolium salts by using a strong base, such as potassium *tert*-butoxide or sodium hydride as deprotonation reagent. Lin et al. [7] reported that Ag–NHC complexes can be synthesized from the addition of imidazolium salt and Ag_2O, and the Ag–NHC complexes formed can readily transfer the NHCs to palladium or rhodium to form Pd–NHC or rhodium–NHC complexes. Crabtree et al. [8] reported that *N*, *N*′-dimethylimidazolium-2-carboxylate can be used as an NHC transfer agent to transition metals.

On the other hand, hydrosilylation is one of the most significant Si–C bond formation reactions in organosilicon chemistry. Many organosilicon monomers containing functional groups have been synthesized via this reaction [9,10]. Apart from platinum complexes, rhodium complexes have been widely applied as highly effective catalysts in hydrosilylation processes [11,12]. Rhodium complexes with phosphine ligands such as $Rh(PPh_3)_3Cl$ are often used. Though the catalytic hydrosilylation process is well established, on the basic of economic criteria concern, further improvement of the catalytic activity and selectivity still remains a big challenge and continues to be the focus of intense research. *N*-heterocyclic carbenes (NHCs) have become universal ligands in organometallic and inorganic coordination chemistry [13–17]. The use of NHCs as replacements for phosphines has provided some significant improvements over traditional phosphine-based ligands [6]. Rhodium complexes such as [RhCl(cod)NHC], [RhCl(CO)NHC], [$RhCl(PPh_3)_2$NHC], etc. as effective catalysts in the hydrosilylation of alkenes and alkynes with silanes have been demonstrated [18–21]. Very recently, a new hydrosilylation process in a $scCO_2$/IL system with a rhodium complex as the catalyst had been reported by our group [22]. During this process, rhodium complexes of NHC were formed by direct carboxylation of 1,3-dialkylimidazolium hexafluorophosphate with CO_2 *in situ*. Herein, we described the synthetic strategy for the preparation of rhodium complexes bearing NHC ligands by using 1-alkyl-3-methylimidazolium-2-carboxylate as NHC transfer agent, and the catalytic activity and selectivity of rhodium complexes prepared in the hydrosilylation of olefins with triethoxysilane in ionic liquid were investigated (Scheme 1).

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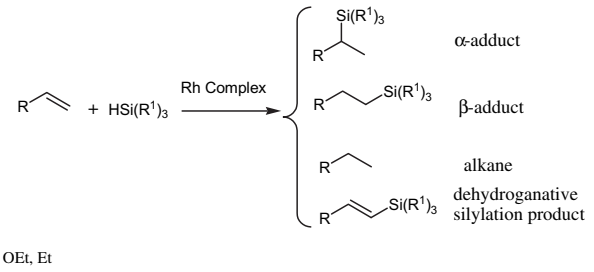


Scheme 1. Hydrosilylation of alkenes with triethoxysilane catalysed by rhodium complex.

2. Experimental sections

2.1. General information

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.

1-Methyl-3-butylimidazolium hexafluorophosphate ($BMimPF_6$) was prepared according to literature procedures [23].

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 and ^{13}C spectra were measured using a Bruker AV400MHz spectrometer operating at 400.13 and 100.62 MHz, respectively.

Elemental analyses were performed on a VARIO EL-3 elemental analyzer.

2.2. Synthesis of 1,3-dialkylimidazolium-2-carboxylates

A screw-top pressure tube was charged with dimethyl carbonate (3.0 mL), 1-alkylimidazole (2.0 mL) and a stir bar. It was sealed and heated for 30–70 h at 80–90 °C to give a brown oil, which was washed with diethyl ether (3 × 10 mL). It was purified by recrystallization in acetonitrile to give a yellow solid, which was dried in vacuo to give the product (Scheme 2).

2.2.1. 1,3-Dimethylimidazolium-2-carboxylate (**1a**)

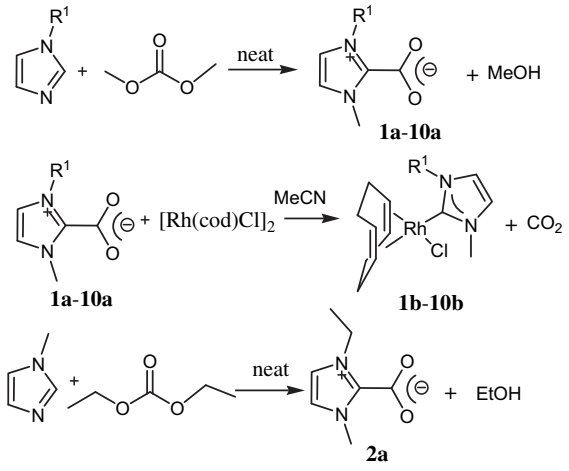
Synthesized by the reaction of 1-methylimidazole and dimethyl carbonate (Yield: 92%). ^1H NMR (400 MHz, D_2O) δ (ppm): 4.00 (s, 6H, N–CH_3), 7.39 (s, 2H, imidazol). Analysis calculated for ($C_6H_8N_2O_2$): C 51.42%; H 5.75%; N 19.99%; O 22.83%. Found: C 51.44%; H 5.76%; N 19.98%; O 22.81%.

2.2.2. 1-Ethyl-3-methylimidazolium-2-carboxylate (**2a**)

Synthesized by the reaction of 1-ethylimidazole and dimethyl carbonate (Yield: 88%) or synthesized by the reaction of 1-methylimidazole and diethyl carbonate (Yield: 45%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.84 (t, J = 8 Hz, 3H, CH_3), 3.84 (s, 3H, N–CH_3), 4.62 (m, 2H, N–CH_2), 7.39 (brs, 1H, imidazol), 7.42 (brs, 1H, imidazol). Analysis calculated for ($C_7H_{10}N_2O_2$): C 54.54%; H 6.54%; N 18.17%; O 20.76%. Found: C 54.51%; H 6.55%; N 18.16%; O 20.78%.

2.2.3. 1-Butyl-3-methylimidazolium-2-carboxylate (**3a**)

Synthesized by the reaction of 1-butylimidazole and dimethyl carbonate (Yield: 86%).^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.74 (t, J = 8 Hz, 3H, CH_3), 1.19–1.70 (m, 4H, CH_2), 3.95 (s, 3H, N–CH_3), 4.14 (m, 2H, N–CH_2), 7.39 (brs, 1H, imidazol), 7.54 (brs, 1H, imidazol). Analysis calculated for ($C_9H_{14}N_2O_2$): C 59.32%; H 7.74%; N 15.37%; O 17.56%. Found: C 59.34%; H 7.70%; N 15.38%; O 17.58%.



Compound	Rhodium NHC	R^1
1a	**1b**	methyl
2a	**2b**	ethyl
3a	**3b**	butyl
4a	**4b**	hexyl
5a	**5b**	2-propenyl
6a	**6b**	phenyl
7a	**7b**	benzyl
8a	**8b**	4-methylphenyl
9a	**9b**	2, 6-diisopropylphenyl
10a	**10b**	2, 4, 6-trimethylphenyl

Scheme 2. Synthesis of imidazolium-2-carboxylates and rhodium *N*-heterocyclic carbene complexes.

2.2.4. 1-Hexyl-3-methylimidazolium-2-carboxylate (**4a**)

Synthesized by the reaction of 1- hexylimidazole and dimethyl carbonate (Yield: 83%).^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.76 (t, J = 8 Hz, 3H, CH_3), 1.05–1.80 (m, 8H, CH_2), 3.87 (s, 3H, N–CH_3), 4.08 (m, 2H, N–CH_2), 7.32 (brs, 1H, imidazol), 7.52 (brs, 1H, imidazol). Analysis calculated for ($C_{11}H_{18}N_2O_2$): C 62.83%; H 8.63%; N 13.32%; O 15.22%. Found: C 62.85%; H 8.58%; N 13.33%; O 15.24%.

2.2.5. 1-(2-Propenyl)-3-methylimidazolium-2-carboxylate (**5a**)

Synthesized by the reaction of 1-(2-Propenyl) imidazole and dimethyl carbonate (Yield: 87%).^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.88 (s, 3H, N–CH_3), 4.93 (m, 2H, N–CH_2), 5.25–5.32 (m, 2H, CH=CH_2), 6.05 (m, 1H, CH=CH_2), 7.34 (brs, 1H, imidazol), 7.56 (brs, 1H, imidazol). Analysis calculated for ($C_8H_{10}N_2O_2$): C 57.82%; H 6.07%; N 16.86%; O 19.26%. Found: C 57.83%; H 6.05%; N 16.87%; O 19.24%.

2.2.6. 1-Phenyl-3-methylimidazolium-2-carboxylate (**6a**)

Synthesized by the reaction of 1-phenylimidazole and dimethyl carbonate (Yield: 66%).^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.84 (s, 3H, N–CH_3), 7.01–7.52 (m, 5H, Ph), 7.37 (brs, 1H, imidazol), 7.39 (brs, 1H, imidazol). Analysis calculated for ($C_{11}H_{10}N_2O_2$): C 65.34%; H 4.98%; N 13.85%; O 15.82%. Found: C 65.31%; H 4.98%; N 13.86%; O 15.85%.

2.2.7. 1-Benzyl-3-methylimidazolium-2-carboxylate (**7a**)

Synthesized by the reaction of 1-benzylimidazole and dimethyl carbonate (Yield: 71%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.84

(s, 3H, N–CH_3), 6.08 (m, 2H, N–CH_2), 7.32–7.52 (m, 5H, Ph), 7.32 (brs, 1H, imidazol), 7.45 (brs, 1H, imidazol).Analysis calculated for ($C_{12}H_{12}N_2O_2$): C 66.65%; H 5.59%; N 12.96%; O 14.80%. Found: C 66.61%; H 5.58%; N 12.98%; O 14.83%.

2.2.8. 1-(4-Methylphenyl)-3-methylimidazolium-2-carboxylate (**8a**)

Synthesized by the reaction of 1-(4-methylphenyl)imidazole and dimethyl carbonate (Yield: 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.25(s, 3H, $PhCH_3$), 3.94 (s, 3H, N–CH_3), 7.15–7.28 (m, 4H, Ph), 7.32 (brs, 1H, imidazol), 7.35 (brs, 1H, imidazol). Analysis calculated for ($C_{12}H_{12}N_2O_2$): C 66.65%; H 5.59%; N 12.96%; O 14.80%. Found: C 66.63%; H 5.59%; N 12.98%; O 14.80%.

2.2.9. 1-(2,6-Diisopropylphenyl)-3-methylimidazolium-2-carboxylate (**9a**)

Synthesized by the reaction of 1-(2,6-diisopropylphenyl)imidazole and dimethyl carbonate (Yield: 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.21(d, J = 8 Hz, 12H, $CH(CH_3)_2$), 2.50(m, 2H, $CH(CH_3)_2$), 3.92 (s, 3H, N–CH_3), 7.32–7.52 (m, 3H, Ph), 7.32 (brs, 1H, imidazol), 7.38 (brs, 1H, imidazol). Analysis calculated for ($C_{17}H_{22}N_2O_2$): C 71.30%; H 7.74%; N 9.78%; O 11.17%. Found: C 71.28%; H 7.74%; N 9.79%; O 11.19%.

2.2.10. 1-(2,4,6-Trimethylphenyl)-3-methylimidazolium-2-carboxylate (**10a**)

Synthesized by the reaction of 1-(2,4,6-trimethylphenyl)imidazole and dimethyl carbonate (Yield: 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):2.09 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 3.88 (s, 3H, N–CH_3), 7.08 (s, 2H, Ph), 7.35 (brs, 1H, imidazol), 7.41 (brs, 1H, imidazol). Analysis calculated for ($C_{14}H_{16}N_2O_2$): C 68.83%; H 6.60%; N 11.47%; O 13.10%. Found: C 68.81%; H 6.59%; N 11.49%; O 13.11%.

These data were consistent with those reported in the literature [24].

2.3. Synthesis of rhodium N-heterocyclic carbene complexes

These compound were prepared by stirring a mixture of 500 mg (1.01 mmol) of bis(η^4-1,5-cyclooctadiene) dichlorodirhodium and 2.2 mmol of 1-alkyl-3–methyl imidazolium-2-carboxylate in 10 mL of acetonitrile in a Schlenk flask for 40 min at room temperature. The reaction mixture was evaporated under reduced pressure and washed with diethyl ether (3 × 10 mL). The yellow solid was dissolved in methylene chloride (2 mL) and purified by repeated recrystallization from diethyl ether.

2.3.1. Chloro(η^4-1,5-cyclooctadiene)(1-methyl-3-methylimidazole-2-ylidene)rhodium(I) (**1b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.72 (s, 2H, imidazol), 4.95 (m, 2H, COD CH), 4.00 (m, 6H, N–CH_3), 3.33 (m, 2H, COD CH), 2.33 (m, 4H, COD CH_2), 1.89 (m, 4H, COD CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.9, 33.0, 37.6(J_{N-C} = 7 Hz), 67.6 (J_{Rh-C} = 15 Hz), 98.5 (J_{Rh-C} = 7 Hz), 121.9, 182.8 (J_{C-Rh} = 50 Hz). Analysis calculated for ($C_{13}H_{20}RhN_2Cl$): C 45.57%; H 5.88%; N 8.18%. Found: C 45.59%; H 5.86%; N 8.19% (Yield: 92%).

2.3.2. Chloro(η^4-1,5-cyclooctadiene)(1-ethyl-3-methylimidazole-2-ylidene)rhodium(I) (**2b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.82 (br d, J = 4 Hz, 2H, imidazol), 5.00 (m, 2H, COD CH), 4.47 (m, 2H, N–CH_2), 3.72 (m, 3H, N–CH_3), 3.29 (m, 1H, COD CH), 3.25 (m, 1H, COD CH), 2.37 (m, 4H, COD CH_2), 1.98 (brm, 4H, 4HCOD CH_2), 1.22 (t, J = 8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.8, 28.5, 32.5, 37.8(J_{N-C} = 7 Hz), 46.6 (J_{N-C} = 10 Hz), 67.1 (d, J_{Rh-C} = 14 Hz), 98.3 (d, J_{Rh-C} = 7 Hz), 120.3, 122.2, 181.9 (d, J_{C-Rh} = 50 Hz). Analysis calculated for ($C_{14}H_{22}RhN_2Cl$): C 47.14%; H 6.22%; N 7.85%. Found: C 47.11%; H 6.22%; N 7.88% (Yield: 88%).

2.3.3. Chloro(η^4-1,5-cyclooctadiene)(1-butyl-3-methylimidazole-2-ylidene)rhodium(I) (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.81 (br d, J = 4 Hz, 2H, imidazol), 5.01 (m, 2H, COD CH), 4.49 (m, 2H, N–CH_2), 4.07 (m, 3H, N–CH_3), 3.34 (m, 1H, COD CH), 3.25 (m, 1H, COD CH), 2.38 (m, 4H, COD CH_2), 1.98 (brm, 6H, 4HCOD CH_2 and 2H Bu CH_2), 1.29 (m, 2H, Bu CH_2), 0.92 (t, J = 8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 18.4, 28.6, 32.6, 33.0, 37.7(J_{N-C} = 7 Hz), 50.5 (J_{N-C} = 10 Hz), 67.2 (d, J_{Rh-C} = 14 Hz), 98.3 (d, J_{Rh-C} = 7 Hz), 120.1, 122.0, 181.8 (d, J_{C-Rh} = 50 Hz). Analysis calculated for ($C_{16}H_{26}RhN_2Cl$): C 49.95%; H 6.81%; N 7.28%. Found: C 49.89%; H 6.90%; N 7.26% (Yield: 88%).

2.3.4. Chloro(η^4-1,5-cyclooctadiene)(1-hexyl-3-methylimidazole-2-ylidene)rhodium(I) (**4b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.81 (br d, J = 4 Hz, 2H, imidazol), 4.92 (m, 2H, COD CH), 4.46 (m, 2H, N–CH_2), 4.07 (m, 3H, N–CH_3), 3.35 (m, 1H, COD CH), 3.24 (m, 1H, COD CH), 2.40 (m, 4H, COD CH_2), 1.29–2.00 (brm, 12H, 4HCOD CH_2 and 8H CH_2), 0.92 (t, J = 8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 11.3, 28.7, 29.8,30.3, 31.1, 32.1, 33.0, 37.8 (J_{N-C} = 7 Hz), 50.2 (J_{N-C} = 10 Hz), 67.6 (d, J_{Rh-C} = 14 Hz), 98.5 (d, J_{Rh-C} = 7 Hz), 120.3, 121.9, 182.1 (d, J_{C-Rh} = 50 Hz). Analysis calculated for ($C_{18}H_{30}RhN_2Cl$): C 52.37%; H 7.33%; N 6.79%. Found: C 52.36%; H 7.31%; N 6.81% (Yield: 84%).

2.3.5. Chloro(η^4-1,5-cyclooctadiene)[1-(2-propenyl)-3-methylimidazole-2-ylidene]rhodium(I) (**5b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.82 (br d, J = 4 Hz, 1H, imidazol), 6.62 (br d, J = 4 Hz, 1H, imidazol), 4.80 (m, 2H, COD CH), 4.15 (m, 2H, 1H N–CH_2 and1H NCH_2CH=CH_2), 3.95 (m, 3H, N–CH_3), 3.67(d, J = 12 Hz, 1H, N–CH_2), 3.32 (m, 1H, COD CH), 3.24 (m, 1H, COD CH), 2.23 (m, 4H, COD CH_2), 2.18–1.87 (brm, 6H, 4HCOD CH_2 and 2H NCH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.4, 32.1, 35.6, 38.1(J_{N-C} = 7 Hz), 47.2, 52.4(J_{N-C} = 10 Hz), 66.5 (d, J_{Rh-C} = 14 Hz), 97.35(d, J_{Rh-C} = 7 Hz), 119.6, 123.2, 182.3 (d, J_{C-Rh} = 50 Hz). Analysis calculated for ($C_{15}H_{22}RhN_2Cl$): C 48.86%; H 6.01%; N 7.60%. Found: C 48.84%; H 6.00%; N 7.62% (Yield: 93%).

2.3.6. Chloro(η^4-1,5-cyclooctadiene)(1-phenyl-3-methylimidazole-2-ylidene)rhodium(I) (**6b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03(m, 2H, Ph), 7.56–7.46 (m, 3H, Ph), 6.97 (br d, J = 4 Hz, 1H, imidazol), 6.82 (br d, J = 4 Hz, 1H, imidazol), 4.60 (m, 2H, COD CH), 4.03 (m, 3H, N–CH_3), 3.28 (m, 1H, COD CH), 3.21 (m, 1H, COD CH), 2.34 (m, 4H, COD CH_2), 1.97 (brm, 4H, 4HCOD CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.5, 32.5, 37.8 (J_{N-C} = 7 Hz), 67.1 (d, J_{Rh-C} = 14 Hz), 98.3 (d, J_{Rh-C} = 7 Hz), 120.1, 122.5, 125.8, 128.8, 129.0, 138.9, 181.9 (d, J_{C-Rh} = 50 Hz), due to overlapping of signals, the carbon resonances from δ 125 to 139 were listed. Analysis calculated for ($C_{18}H_{22}RhN_2Cl$): C 53.42%; H 5.48%; N 6.92%. Found: C 53.40%; H 5.48%; N 6.93% (Yield: 89%).

2.3.7. Chloro(η^4-1,5-cyclooctadiene)(1-benzyl-3-methylimidazole-2-ylidene)rhodium(I) (**7b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56–7.26 (m, 5H, Ph), 6.87 (br d, J = 4 Hz, 1H, imidazol), 6.60 (br d, J = 4 Hz, 1H, imidazol), 5.58 (br s, 2H, CH_2Ph), 4.87 (m, 2H, COD CH), 4.23 (m, 3H, N–CH_3), 3.29 (m, 1H, COD CH), 3.25 (m, 1H, COD CH), 2.38 (m, 4H, COD CH_2), 1.95 (brm, 4H, 4HCOD CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.8, 32.1, 37.8 (J_{N-C} = 7 Hz), 54.6(J_{N-C} = 11 Hz), 67.3 (d, J_{Rh-C} = 14 Hz), 98.7 (d, J_{Rh-C} = 7 Hz), 119.9, 121.3, 128.1, 128.3, 129.0, 135.6181.9 (d, J_{C-Rh} = 50 Hz). Analysis calculated for ($C_{19}H_{24}RhN_2Cl$): C 54.49%; H 5.78%; N 6.69%. Found: C 54.47%; H 5.77%; N 6.69% (Yield: 89%).

*2.3.8. Chloro(η^4-1,5-cyclooctadiene)[1-(4-methylphenyl)-3-methylimidazole-2-ylidene]rhodium(I) (**8b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.26–7.92(m, 4H, Ph), 6.99 (br d, J = 4 Hz, 1H, imidazol), 6.88 (br d, J = 4 Hz, 1H, imidazol), 4.64 (m, 2H, COD CH), 4.13 (m, 3H, N–CH_3), 3.18 (m, 1H, COD CH), 3.23 (m, 1H, COD CH), 2.33(s, 3H, PhCH_3), 2.01 (m, 4H, COD CH_2), 1.87 (brm, 4H, 4HCOD CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.1, 27.9, 32.8, 38.8(J_{N-C} = 7 Hz), 67.6 (d, J_{Rh-C} = 14 Hz), 97.7 (d, J_{Rh-C} = 7 Hz), 121.1, 122.7, 127.7, 131.6, 133.3, 138.9183.9 (d, J_{C-Rh} = 50 Hz), due to overlapping of signals, the carbon resonances from δ 125 to 139 were listed. Analysis calculated for ($C_{19}H_{24}RhN_2Cl$): C 54.49%; H 5.78%; N 6.69%. Found: C 54.47%; H 5.78%; N 6.70% (Yield: 89%).

*2.3.9. Chloro(η^4-1,5-cyclooctadiene)[1-(2,6-diisopropylphenyl)-3-methylimidazole-2-ylidene]rhodium(I) (**9b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.17–7.35(m, 3H, Ph), 6.99 (br d, J = 4 Hz, 1H, imidazol), 6.83 (br d, J = 4 Hz, 1H, imidazol), 4.66 (m, 2H, COD CH), 4.13 (m, 3H, N–CH_3), 3.26 (m, 1H, COD CH), 3.14 (m, 1H, COD CH), 2.93 (m, 2H, $CH(CH_3)_2$), 2.13 (m, 4H, COD CH_2), 1.97 (brm, 4H, 4HCOD CH_2), 1.23(d, J = 8 Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.6, 26.0, 28.7, 33.4, 37.8(J_{N-C} = 7 Hz), 68.3 (d, J_{Rh-C} = 14 Hz), 98.1 (d, J_{Rh-C} = 7 Hz), 121.7, 122.8, 123.7, 125.9, 130.0, 134.2181.9 (d, J_{C-Rh} = 50 Hz), due to overlapping of signals, the carbon resonances from δ 125 to 139 were listed. Analysis calculated for ($C_{24}H_{34}RhN_2Cl$): C 58.96%; H 7.01%; N 5.73%. Found: C 58.97%; H 7.00%; N 5.72% (Yield: 84%).

*2.3.10. Chloro(η^4-1,5-cyclooctadiene)[(2,4,6-trimethylphenyl)-3-methylimidazole-2-ylidene]rhodium(I) (**10b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.06(s, 2H, Ph), 6.99 (br d, J = 4 Hz, 1H, imidazol), 6.83 (br d, J = 4 Hz, 1H, imidazol), 4.46 (m, 2H, COD CH), 4.23 (m, 3H, N–CH_3), 3.30 (m, 1H, COD CH), 3.26 (m, 1H, COD CH), 2.32 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.02 (m, 4H, COD CH_2), 1.61 (brm, 4H, 4HCOD CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.5, 20.0, 21.4, 28.5, 32.5, 37.8(J_{N-C} = 7 Hz), 68.7 (d, J_{Rh-C} = 14 Hz), 96.3 (d, J_{Rh-C} = 7 Hz), 122.1, 124.5, 125.3, 128.8, 137.0, 138.4, 183.5 (d, J_{C-Rh} = 50 Hz), due to overlapping of signals, the carbon resonances from δ 125 to 139 were listed. Analysis calculated for ($C_{21}H_{28}RhN_2Cl$): C 56.45%; H 6.32%; N 6.27%. Found: C 56.44%; H 6.31%; N 6.29% (Yield: 87%).

These data were consistent with those reported in the literature [24].

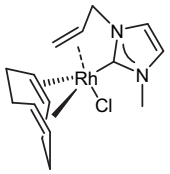
2.4. Catalytic hydrosilylation of alkene with triethoxysilane

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 triethoxysilane

2.4.1.1. 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).

2.4.1.2. 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).



5b

Scheme 3. Complex **5b**.

2.4.1.3. 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 reaction of styrene with triethylsilane

2.4.2.1. β-Adduct [triethyl(phenethyl)silane]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.66 (q, J = 8 Hz, 6H, Si–CH_2), 092 (t, J = 8 Hz, 9H, CH_3), 0.98 (t, J = 8 Hz, 2H, Si–CH_2), 2.71 (t, J = 8 Hz, 2H, CH_2), 7.11–7.27 (m, 5H, Ph).

2.4.2.2. α-Adduct [triethyl(1-phenylethyl)silane]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.69 (q, J = 8 Hz, 6H, Si–CH_2), 097 (t, J = 8 Hz, 9H, CH_3), 1.21 (d, J = 9 Hz, 3H, CH_3), 3.58 (q, J = 8 Hz, 6H, O–CH_2), 7.15–7.23 (m, 5H, Ph).

2.4.2.3. Dehydrogenative silylation product [triethyl(styryl)silane]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.93 (t, J = 9 Hz, 9H, CH_3), 1.33 (q, J = 8 Hz, 6H, Si–CH_2), 6.47 (d, J = 12 Hz, 1H, SiCH), 6.98(d, J = 12 Hz, 1H, CHPh), 7.16–7.34 (m, 5H, Ph).

2.4.3. Hydrosilylation of 1-hexene with triethoxysilane

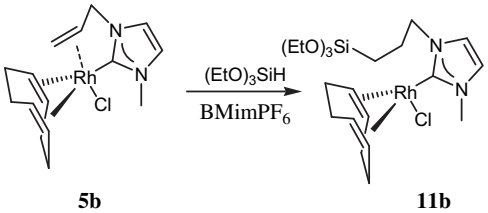
2.4.3.1. β-Adduct (hexyltriethoxysilane). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.64 (t, J = 6 Hz, 2H, Si–CH_2), 0.89 (t, J = 8 Hz, 3H, CH_3), 1.22–1.42 (m, 17H, CH_2 CH_3), 3.81 (q, J = 8 Hz, 6H, O–CH_2).

These data were consistent with those reported in the works [12,22].

*2.4.4. Chloro(η^4-1,5-cyclooctadiene){1-[3-(triethoxysilyl)propyl]-3-methylimidazole-2-ylidene}rhodium(I) (**11b**)*

At the end of the reaction, the catalyst phase (**5b**/$BMimPF_6$) was separated from the product by decantation and the structure was determined by ^{1}H NMR (Scheme 4).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.02 (br d, J = 4 Hz, 1H, imidazol), 6.81 (br d, J = 4 Hz, 1H, imidazol), 4.82 (m, 2H, COD CH), 4.24(m, 2H, N–CH_2), 3.93 (m, 3H, N–CH_3), 3.82 (q, J = 8 Hz, 6H, O–CH_2), 3.31 (m, 1H, COD CH), 3.24 (m, 1H, COD CH), 2.21 (m, 4H, COD CH_2), 2.18–1.87 (brm, 4H, 4HCOD CH_2), 1.64–1.12 (m, 11H, CH_2 CH_3), 0.71(t, J = 6 Hz, 2H, Si–CH_2)/$BMimPF_6$: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.49 (s, 1H, imidazol), 7.33–7.29 (m, 2H, imidazol), 4.17 (t, J = 8 Hz, 2H, N–CH_2), 3.95 (s, 3H, N–CH_3), 1.87–1.22(m, 4H, CH_2), 0.95 (t, J = 8 Hz, 3H, CH_3).



5b **11b**

Scheme 4. Complex **11b**.

3. Results and discussion

3.1. Synthesis and characterization of 1-alkyl-3-methylimidazolium-2-carboxylate

There are only a few literatures concerning imidazolium-2-carboxylates. In 1974, Schlösser and Regitz [25] first isolated 1, 3-diphenylimidazolinium-2-carboxylate by hydrolysis of more complex zwitterionic carbamate derivatives. Kuhn et al. [26] used CO_2 to trap 1, 3-diisopropyl-4, 5-dimethylimidazol-2-ylidene as stable adduct in 1999. In 2005, Crabtree et al. [8,24] showed that *N*, *N*′-dimethylimidazolium-2-carboxylate can be an NHC transfer agent to transition metals. And the syntheses of *N*, *N*′-dimethylimidazolium-2-carboxylate usually use base and in some cases a high pressure of CO_2. But the experimental procedure did not easily operate and hard to isolate product. In 2003, Tkatchenko and co-workers [27] reported the formation of 1,3-dimethylimidazolium-2-carboxylate from 1-methylimidazole and dimethyl carbonate. In 2005, Tommasi and Crabtree [8,24] subsequently extended the procedure to the preparation of 1-butyl-3-methylimidazolium-2-carboxylate. But this method that was limited to the preparation of 1,3-dimethylimidazolium-2-carboxylate and 1-butyl-3-methylimidazolium-2-carboxylate was only reported in a few literatures. We have extended this procedure to the preparation of 1-alkyl-3-methylimidazolium-2-carboxylate. A series of 1-alkyl-3-methylimidazolium-2-carboxylate (**2a**–**10a**) were synthesized by the reaction of 1-alkylimidazole and dimethyl carbonate. At the same time, we find that 1-ethyl-3-methylimidazolium-2-carboxylate could also be synthesized by the reaction of 1-methylimidazole and diethyl carbonate. These ten products are characterized by NMR spectroscopy and elemental analysis. And the NMR spectroscopy and elemental analysis data of the prepared compounds are in agreement with the assigned structures.

3.2. Synthesis and characterization of rhodium N-heterocyclic carbene complexes

1-Allyl-3-methylimidazolium-2-carboxylate, air- and moisture-stable species, can transfer NHCs to $[Rh(cod)Cl]_2$ with release of CO_2. For example, chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazole-2-ylidene)rhodium(I) (**1b**) was synthesized by the 1,3-dimethylimidazolium-2-carboxylate reacts and $[Rh(cod)Cl]_2$; chloro (η^4-1,5-cyclooctadiene)[1-phenyl-3-methylimidazole-2-ylidene] rhodium(I) (**6b**) was synthesized by the 1-phenyl-3-methylimidazolium-2-carboxylate reacts and $[Rh(cod)Cl]_2$. **1b** was obtained in 92% isolated yield and **6b** was obtained in 89% isolated yield.

And a series of rhodium complexes bearing NHC ligands were synthesized by this way and characterized by NMR spectroscopy and elemental analysis. The NMR spectroscopy (^{1}H NMR and ^{13}C NMR) and elemental analysis data of the prepared compounds were in agreement with the assigned structures.

The chloro(η^4-1,5-cyclooctadiene)[1-(2-propenyl)-3-methylimidazole-2-ylidene]rhodium(I) (**5b**) was synthesized by the reaction of the 1-(2-propenyl)-3-methylimidazolium-2-carboxylate and $[Rh(cod)Cl]_2$ for the first time. We find η^2-coordination mode of **5b** (Scheme 3) in CD_3Cl is visible in the NMR spectroscopy (^{1}H NMR). The signals for the protons of the allylic double bond in **5b** are significantly shifted to higher field compared to compound **5a**. The allylic CH and CH_2 resonances appear at $\delta = 6.05$ and $\delta = 5.25$–5.32 ppm for **5a** and at $\delta = 4.15$ and $\delta = 1.87$–2.18 ppm for **5b**, respectively. Upon coordination of the allylic double bond, the N–CH_2 protons of this group become enatiotopic and give rise to two signals at $\delta = 4.15$ and 3.67 ppm, while the spectrum of compound **5a** exhibits only one resonance for allylic N–CH_2 protons $\delta = 4.93$ ppm.

Table 1
Synthesis of imidazolium-2-carboxylates and rhodium *N*-heterocyclic carbene complexes.

Entry	a	Material		Yield[a] (%)	b	Yield[a] (%)
1	**1a**	1-Methylimidazole	Dimethyl carbonate	92	**1b**	92
2	**2a**	1-Ethylimidazole		88	**2b**	88
3	**3a**	1-Butylimidazole		86	**3b**	88
4	**4a**	1-Hexylimidazole		83	**4b**	84
5	**5a**	1-(2-Propenyl) imidazole		87	**5b**	93
6	**6a**	1-Phenylimidazole		66	**6b**	89
7	**7a**	1-Benzylimidazole		71	**7b**	89
8	**8a**	1-(4-Methylphenyl) imidazole		67	**8b**	89
9	**9a**	1-(2,6-Diisopropyl phenyl) imidazole		62	**9b**	84
10	**10a**	1-(2,4,6-Tri methylphenyl)imidazole		64	**10b**	87
11	**2a**	1-Methylimidazole	Diethyl carbonate	45	**2b**	88

[a] Isolated yields.

3.3. Hydrosilylation catalysed by rhodium N-heterocyclic carbene complexes in the ionic liquid medium

Recently, our group [22] reports a new hydrosilylation process in a $scCO_2$/IL system with a rhodium complex as the catalyst. During this process, Rh complexes of NHCs exhibited excellent catalytic activity and selectivity was synthesized by direct carboxylation of 1,3-dialkylimidazolium hexafluorophosphate with CO_2 *in situ*. In order to research effect of Rhodium complexes bearing NHC ligands, we had synthesized a series of rhodium complexes bearing NHC ligands. The results listed in Table 1 indicate that $Rh(PPh_3)_3Cl$ and

Table 2
Effect of the catalyst/IL system on the hydrosilylation reaction of styrene with triethoxysilane.

Entry	Catalyst (substrate mol %)	$BMimPF_6$ (mL)	Conv. (%)	Select. (%)			Ton
				β	α	Byproduct	
1	$Rh(PPh_3)_3Cl$ 0.1	2	78.1	81.2	16.5	2.3[a]	781
2	$[Rh(cod)Cl]_2$ 0.05	2	45.6	59.1	39.8	1.1[a]	456[b]
3	**1b** 0.1	2	91.3	54.1	45.9	–	913
4	**2b** 0.1	2	88.8	59.4	40.6	–	888
5	**3b** 0.1	2	86.4	64.7	35.3	–	864
6	**4b** 0.1	2	84.5	70.3	29.7	–	845
7	**5b** 0.1	2	89.1	86.8	13.2	–	911
8	**6b** 0.1	2	88.2	84.5	15.5	–	882
9	**7b** 0.1	2	93.5	82.1	17.9	–	935
10	**8b** 0.1	2	94.9	87.5	12.5	–	949
11	**9b** 0.1	2	95.6	91.5	8.5	–	956
12	**10b** 0.1	2	96.8	90.2	9.8	–	968
13	**10b** 0.5	2	100	89.7	10.3	–	200
14	**10b** 0.2	2	98.2	90.0	10.0	–	491
15	**10b** 0.05	2	79.1	90.7	9.3	–	1582
16	**10b** 0.1	4	97.0	90.2	9.8	–	970
17	**10b** 0.1	6	96.9	90.3	9.7	–	969
18[c]	**10b** 0.1	2	93.8	90.1	9.9	–	938
19[d]	**10b** 0.1	2	93.6	90.4	9.6	–	936
20[e]	**10b** 0.1	2	93.4	90.3	9.7	–	934
21[f]	**10b** 0.1	2	93.1	90.4	9.6	–	931
22[g]	**10b** 0.1	2	92.4	90.6	9.4	–	924

Reaction conditions: styrene 30 mmol; triethoxysilane 36 mmol; 70 °C; 2 h.
Byproduct: ethylbenzene and unsaturated-adduct.
[a] Ethylbenzene.
[b] Based on Rh.
[c] Second run.
[d] Third run.
[e] Fourth run.
[f] Fifth run.
[g] Sixth run.

Table 3
Results of the hydrosilylation reaction of other alkenes with triethoxysilane.

Entry	Alkene	Silane	Conv. (%)	Selectivity (%)			Ton
				β	α	Byproduct	
1	1-Hexene	Triethoxysilane	100	100	–	–	5000
2	1-Heptene		100	100	–	–	5000
3	1-Octene		~100	100	–	–	~5000
4	1-Dodecene		99.9	100	–	–	4995
5[a]	2-Methyl-styrene		94.2	92.3	7.7	–	1796
6[a]	4-Methyl-styrene		97.4	89.7	10.3	–	1874
7[a]	4-Methoxy-styrene		98.1	87.1	12.9	–	1916
8[a]	4-Fluoro-styrene		97.1	90.7	9.3	–	1882
9[a]	4-Chloro-styrene		96.9	91.4	8.6	–	1872
10[b]	Styrene	Triethylsilane	99.1	71.7	4.2	24.1	991

Reaction conditions: alkene 30 mmol; triethoxysilane 36 mmol; **10b** 0.02 mol% of styrene; $BMimPF_6$ 2 mL; 70 °C; 2 h.
[a] Reaction conditions: styrene 30 mmol; triethoxysilane 36 mmol; **10b** 0.1 mol% of styrene; $BMimPF_6$ 2 mL; 70 °C; 2 h.
[b] Reaction conditions: styrene 30 mmol; triethylsilane 36 mmol; **10b** 0.1 mol% of styrene; $BMimPF_6$ 2 mL; 70 °C; 2 h. Byproduct: dehydrogenative silylation product; no alkane.

$[Rh(cod)Cl]_2$ had low catalytic activity and selectivity in $BMimPF_6$, respectively. In contrast to $Rh(PPh_3)_3Cl$ and $[Rh(cod)Cl]_2$, no by-product was detected when chloro(η^4-1,5-cyclooctadiene)(1-alkyl-3-methylimidazole-2-ylidene)rhodium(I) was used as catalyst. The **1b**–**4b** had higher catalytic activity and lower selectivity of the β-adduct in $BMimPF_6$, respectively. And the catalytic activities of rhodium complexes bearing NHC ligands slightly decreased with increasing length of alkyl chain of *N*-substituents, the ratio of the β-adduct to the α-adduct clearly increased. The **5b** had exhibited higher selectivity of the β-adduct and high catalytic activity in $BMimPF_6$ than that of **1b**–**4b**. However, the disappearance of vinyl group in the rhodium complex after the catalytic reaction was detected, and β-silyl-substituted NHC (**11b**) was formed. We also found **6b**–**10b** had higher catalytic activity and higher selectivity of the β-adduct in $BMimPF_6$, respectively. In particular, **10b** and **11b** were obtained >95% conversion of styrene, and >90% selectivity of the β-adduct. It was possible that interaction between the *N*-substituents attached to the NHCs and the central metal rhodium could weaken the complexation abilities of other ligands, such as Cl^-, etc., then that could help to activate the alkene. At the same time, *N*-substituents attached to the NHCs could stabilize the intermediate states, and help to raise the activity of the central metal Rh. The different *N*-substituents attached to the NHCs resulted in different steric hindrance of catalytic center. Therefore, selectivity of the β-adduct could be different [28].

The conversion of styrene increased with increasing amounts of **10b**, the selectivity of the β-adduct was decreased slightly (Table 2, entries 12–15). Meanwhile, the amount of $BMimPF_6$ used had no effect on the conversion of styrene or the selectivity of the β-adduct (Table 2, entries 16–17).

When other alkenes such as 1-hexene, 1-heptene, 1-octene, 1-dodecene, 2-methyl-styrene, 4-methyl-styrene, 4-methoxy-styrene, 4-fluoro-styrene and 4-chloro-styrene replaced styrene as one of the substrates, high levels of conversion and selectivity were obtained with **10b**/$BMimPF_6$ system (Table 3). And when triethylsilane replaced triethoxysilane as one of the substrates, dehydrogenative silylation product [triethyl(styryl)silane] was found [12,22].

Rhodium complexes bearing NHC ligands (**1b**–**4b**, **6b**–**10b**) showed a pronounced solubility in $BMimPF_6$. They were specially designed to be used in ionic liquid biphasic systems and had been employed to circumvent catalyst problems. **10b** in $BMimPF_6$ could be reused without noticeable loss of catalytic activity and selectivity (Table 2, entries 18–22).

4. Conclusion

In summary, a series of 1-alkyl-3-methylimidazolium-2-carboxylate was synthesized by the reaction of 1-alkylimidazole and dimethyl carbonate. 1-Alkyl-3-methylimidazolium-2-carboxylate, air- and moisture-stable species, could transfer NHCs to $[Rh(cod)Cl]_2$ with release of CO_2, and a series of rhodium complexes bearing NHC ligands are synthesized. The catalytic properties of rhodium complexes prepared in the hydrosilylation of alkenes in ionic liquid media were investigated. It was found that both the catalytic activity and selectivity of the rhodium complexes bearing NHC ligands were influenced by the attached substituents of the imidazolium cation. Additionally, rhodium complexes bearing NHC ligands in ionic liquid $BMimPF_6$ could be reused without noticeable loss of catalytic activity and selectivity.

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References

[1] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39–91.
[2] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1992) 361–363.
[3] V. Nair, S. Bindu, V. Sreekumar, Angew. Chem. Int. Ed. 43 (2004) 5130–5135.
[4] D. Enders, T. Balensiefer, Acc. Chem. Res. 37 (2004) 534–541.
[5] A. Tudose, A. Demonceau, D. Lionel, J. Organomet. Chem. 691 (2006) 5356–5365.
[6] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290–1309.
[7] I.J.B. Lin, C.S. Vasam, Comments Inorg. Chem. 25 (2004) 75–129.
[8] A.M. Voutchkova, L.N. Appelhans, A.R. Chianese, R.H. Crabtree, J. Am. Chem. Soc. 127 (2005) 17624–17625.
[9] B. Marciniec, J. Gulinski, J. Organomet. Chem. 253 (1983) 349–362.
[10] I. Ojima, S. Patai, Z. Rappaport, The Chemistry of Organic Silicon Compounds. Wiley–Interscience, New York, 1989, p. 1479 (Chapter 25).
[11] J.V.D. Broeke, F. Winter, B.J. Deelman, G.V. Koten, Org. Lett. 4 (2002) 3851–3854.
[12] J. Li, J. Peng, Y. Bai, G. Zhang, G. Lai, X. Li, J. Organomet. Chem. 695 (2010) 431–436.
[13] V. Cesar, S. Bellemin-Laponnaz, L.H. Gade, Chem. Soc. Rev. 33 (2004) 619–636.
[14] T.J. Katz, Angew. Chem. Int. Ed. 44 (2005) 3010–3019.
[15] J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978–4008.
[16] J. Bosson, S.P. Nolan, J. Org. Chem. 75 (2010) 2039–2043.
[17] G.C. Vougioukalakis, R.H. Grubbs, Chem. Rev. 110 (2010) 1746–1787.
[18] J.E. Hill, T.A. Nile, J. Organomet. Chem. 137 (1977) 293–299.
[19] M.F. Lappert, R.K. Maskell, J. Organomet. Chem. 264 (1984) 217–228.
[20] J.W. Faller, D.G. D'Alliessi, Organometallics 21 (2002) 1743–1746.
[21] M.V. Jiménez, J.J. Pérez-Torrente, M.I. Bartolomé, V. Gierz, F.J. Lahoz, L.A. Oro, Organometallics 27 (2008) 224–234.
[22] J. Li, J. Peng, G. Zhang, Y. Bai, G. Lai, X. Li, New J. Chem. 34 (2010) 1330–1334.
[23] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, J. Dupont, Polyhedron 15 (1996) 1217–1219.
[24] A.M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R.H. Crabtree, J. Am. Chem. Soc. 129 (2007) 12834–12846.
[25] W. Schlösser, M. Regitz, Chem. Ber. 107 (1974) 1931–1948.
[26] N. Kuhn, M. Steimann, G. Weyers, Z. Naturforsch. 54b (1999) 427–433.
[27] J.D. Holbrey, W.M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R.D. Rogers, Chem. Commun. (2003) 28–29.
[28] J.J. Peng, J.Y. Li, Y. Bai, W.H. Gao, H.Y. Qiu, H. Wu, Y. Deng, G.Q. Lai, J. Mol. Catal. A: Chem. 278 (2007) 97–101.