Hydrosilylation catalysed by a rhodium complex in a supercritical CO_2/ionic liquid system

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The hydrosilylation of alkenes in a supercritical CO_2 ($scCO_2$)/ionic liquid (IL) system was investigated. $Rh(PPh_3)_3Cl$ exhibited excellent catalytic activity and selectivity. KO^tBu was used as an additive, and no hydrogenation by-product (alkane) was detected in the $scCO_2$/IL system. During hydrosilylation in the $scCO_2$/IL system, the reactants were possibly transferred into the IL phase by $scCO_2$, in which the catalyst was dissolved. The products can be flushed with $scCO_2$ after the reaction and the catalyst/IL system reused.

1. Introduction

A great deal of research had been devoted to the use of $scCO_2$ for the extraction of useful materials, such as oils, from natural products.[1–3] $ScCO_2$ is an inexpensive, environmentally benign alternative to conventional solvents for chemical synthesis.[4–6] Room temperature ionic liquids (ILs), which consist entirely of ions, have attracted much interest as novel, environmentally friendly benign media in catalyst systems. Many organic reactions had been performed in ILs with excellent yields and chemo- and/or enantioselectivity.[7,8] There are only a few examples of hydrosilylation using ILs.[9–13] Recently, our group[14] reported that $Rh(PPh_3)_3Cl$/IL (molten salt) could be used in the hydrosilylation process as a thermoregulated and recyclable catalyst system that combines the advantages of an IL with convenient product separation. Very recently, the first industrial application of hydrosilylation catalysis in ILs for synthesis of organofunctional silanes was reported.[13]

Carbon dioxide under supercritical conditions ($scCO_2$) has dual properties; it behaves as a gas with high diffusivity and as a liquid with high solubility, which enables $scCO_2$ to diffuse easily through complex matrices and extract the desired substances. $scCO_2$ combined with an IL had been studied by Brennecke *et al.*, who showed that CO_2 could be dissolved significantly into the lower IL phase, but that no polar IL could be dissolved into the $scCO_2$ phase.[15] Therefore, it is expected that the reaction performance will differ with CO_2 dissolved in different ILs.[16,17] Here, we describe a new hydrosilylation process in a $scCO_2$/IL system with a rhodium complex as the catalyst. During this process, 1,3-dialkylimidazolium-2-carboxylates, which are used as *N*-heterocyclic carbene (NHC) ligand precursors, were synthesized by the direct carboxylation of 1,3-dialkylimidazolium hexafluorophosphates with CO_2.

2. Results and discussion

The hydrosilylation reaction (Fig. 1) was performed in 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$). Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, showed a low level of catalytic activity (Table 1, entry 1). A high level of conversion was obtained in the $scCO_2$ system, but only a low level of selectivity for the β-adduct was obtained (Table 1, entry 2). However, both higher catalytic activity and selectivity for the β-adduct were obtained when the hydrosilylation reaction was undertaken in the $scCO_2$/$BMImPF_6$ biphasic system with $Rh(PPh_3)_3Cl$ as the catalyst (Table 1, entry 3). In comparison with $scCO_2$/$BMImPF_6$, when the hydrosilylation reaction was performed in $scCO_2$/1-methyl-3-hexylimidazolium hexafluorophosphate ($HMImPF_6$), lower levels of styrene conversion and higher levels of β-adduct selectivity were obtained. Lower conversion and selectivity were obtained in the tetrafluoroborate anion-based IL $BMImBF_4$ than in $BMImPF_6$. Our conjecture is that the counterion BF_4^- is more nucleophilic than PF_6^-, and so it reduced the solubility of the silane in the hydrophilic IL $BMImBF_4$. Higher conversion and selectivity were obtained in the $scCO_2$/$BMImBF_4$ system than in the $BMImBF_4$ system (Table 1, entries 12 and 13). $scCO_2$ can be used to extract high boiling point organic substances from ILs without cross-contamination of the extract with the IL. During hydrosilylation in the $scCO_2$/IL system, the reactants were possibly transferred into the IL phase by $scCO_2$, in which the catalyst was dissolved. The products can be flushed with $scCO_2$ after the reaction. Therefore, the results show that a high level of conversion was obtained in the presence of $scCO_2$. Furthermore, the by-product (ethylbenzene) was not detected when KO^tBu was added (Table 1, entry 4). It is possible that a rhodium *N*-heterocyclic carbene complex was formed in the hydrosilylation reaction.[18] 1-Methyl-3-butylimidazolium-2-carboxylate was synthesized by the direct carboxylation of 1-methyl-3-butylimidazolium hexafluorophosphate with CO_2 in the presence of KO^tBu, and then

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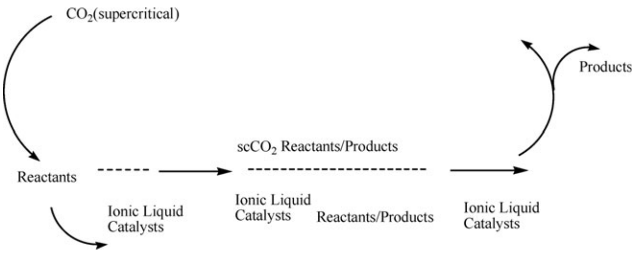


Fig. 1 Hydrosilylation in a supercritical CO$_2$/IL system.

1-methyl-3-butylimidazolium-2-carboxylate as an *N*-heterocyclic carbene precursor was reacted with bis(1,5-cyclooctadiene)-dichlorodirhodium to form [chloro(1,5-cyclooctadiene)(1-butyl-3-methylimidazole-2-ylidene)rhodium(I)], which was an efficient catalyst for the hydrosilylation reaction. The spectroscopic data (^{1}H NMR and ^{13}C NMR) and elemental analysis data of [chloro(1,5-cyclooctadiene)(1-butyl-3-methylimidazole-2-ylidene)rhodium(I)], and the spectroscopic data (^{1}H NMR) of 1-methyl-3-butylimidazolium-2-carboxylate, were in agreement with the assigned structures. Additionally, the results presented in Table 1 show that the catalytic activity of $[Rh(cod)Cl]_2$ was much lower than that of $Rh(PPh_3)_3Cl$ in the scCO$_2$/BMImPF$_6$ system (Table 1, entries 4 and 7). The role of PPh$_3$ is thought to improve the catalytic activity and selectivity of the rhodium complex. When other bases, such as NaOH, replaced KO^{t}Bu, the by-product (ethylbenzene) was obtained.

Although the results listed in Table 1 indicate that the conversion of styrene increased with increasing amounts of $Rh(PPh_3)_3Cl$, the selectivity for the β-adduct decreased slightly. Meanwhile, the amount of BMImPF$_6$ used had no effect on the conversion of styrene or the selectivity for the β-adduct (Table 1, entries 7–9).

In addition, it was found that the catalytic activity of $Rh(PPh_3)_3Cl$ and $[Rh(cod)Cl]_2$ decreased with increasing length of the alkyl chain linked to the *N*,*N*-dialkylimidazolium cation in the scCO$_2$/IL system. In contrast, the selectivity for the β-adduct clearly increased. In particular, a 98.7% selectivity for the β-adduct was achieved when scCO$_2$/1-butyl-3-octylimidazolium hexafluorophosphate (OBImPF$_6$) was used as the reaction medium. This result indicates that the substituents attached to the *N*,*N*-dialkylimidazolium cation have a strong impact on the catalytic process.

During hydrosilylation in the scCO$_2$/IL system, the rhodium complexes were insoluble in scCO$_2$ but soluble in the IL. The reactants were transferred into the IL phase by scCO$_2$, in which the catalyst was dissolved. The product can be flushed with scCO$_2$ after the reaction and the catalyst then reused. The results of catalyst recycling are shown in Table 2. Although the conversion in the recycling experiments decreased from 91.3 to 78.5% over four cycles, the selectivity for the β-adduct remained constant at 86.7%.

The effect of reaction temperature on the hydrosilylation is illustrated in Table 3. The results indicate that the conversion of styrene increases with increasing reaction temperature, whereas the selectivity for the β-adduct decreased with increasing reaction temperature.

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 $Rh(PPh_3)_3Cl$–KO^{t}Bu in the scCO$_2$/BMImPF$_6$ system (Table 4). Also, when triethylsilane replaced triethoxysilane as one of the substrates, unsaturated adduct triethyl(styryl)silane was found, because triethylsilane is easier to dehydrogenate than triethoxysilane. When KO^{t}Bu was added to the system of styrene with triethylsilane, no ethylbenzene was detected in the scCO$_2$/BMImPF$_6$.

3. Experimental

3.1 General methods

Styrene was washed with 5% (w/v) NaOH and dried over Na_2SO_4. After filtration, the styrene was distilled under reduced pressure. All other substances were purchased from Aldrich and used as received. $Rh(PPh_3)_3Cl$ and $[Rh(cod)Cl]_2$ were prepared as previously described.[19]

1-Butyl-3-methylimidazolium hexafluorophosphate (BMImPF$_6$), 1-hexyl-3-methylimidazolium hexafluorophosphate

Table 1 Effect of the scCO$_2$/IL system on the hydrosilylation reaction of styrene with triethoxysilane[a]

						Selectivity (%)			
Entry	Catalyst (mol%)	Co-catalyst	Solvent (mL)	Co-solvent	Conversion (%)	β	α	By-product[b]	TON
1	$RhCl(PPh_3)_3$ (0.1)	—	BMImPF$_6$ (2)	—	78.1	81.2	16.5	2.3	781
2	$RhCl(PPh_3)_3$ (0.05)	—	scCO$_2$	—	92.5	49.7	48.3	2.0	1850
3	$RhCl(PPh_3)_3$ (0.05)	—	BMImPF$_6$ (2)	scCO$_2$	91.6	81.3	16.7	2.0	1832
4	$[RhCl(COD)]_2$ (0.025)	KO^{t}Bu	BMImPF$_6$ (2)	scCO$_2$	73.9	62.0	38.0	—	1478
5	$RhCl(PPh_3)_3$ (0.1)	KO^{t}Bu	BMImPF$_6$ (2)	scCO$_2$	100	84.5	15.5	—	1826
6	$RhCl(PPh_3)_3$ (0.02)	KO^{t}Bu	BMImPF$_6$ (2)	scCO$_2$	54.3	86.3	13.7	—	2715
7	$RhCl(PPh_3)_3$ (0.05)	KO^{t}Bu	BMImPF$_6$ (2)	scCO$_2$	91.3	85.8	14.2	—	1826
8	$RhCl(PPh_3)_3$ (0.05)	KO^{t}Bu	BMImPF$_6$ (4)	scCO$_2$	91.5	85.6	14.4	—	1830
9	$RhCl(PPh_3)_3$ (0.05)	KO^{t}Bu	BMImPF$_6$ (6)	scCO$_2$	91.4	85.9	14.1	—	1828
10	$RhCl(PPh_3)_3$ (0.05)	—	HMImPF$_6$ (2)	scCO$_2$	89.4	84.4	11.3	4.3	1788
11	$RhCl(PPh_3)_3$ (0.05)	KO^{t}Bu	HMImPF$_6$ (2)	scCO$_2$	89.1	89.2	10.8	—	1782
12	$RhCl(PPh_3)_3$ (0.05)	—	BMImBF$_4$ (2)	—	66.4	75.4	15.6	9.0	1328
13	$RhCl(PPh_3)_3$ (0.05)	KO^{t}Bu	BMImBF$_4$ (2)	scCO$_2$	84.2	83.2	16.8	—	1684
14	$RhCl(PPh_3)_3$ (0.05)	NaOH	BMImPF$_6$ (2)	scCO$_2$	90.4	81.5	15.8	2.7	1808

[a] Reaction conditions: styrene 30 mmol, triethoxysilane 36 mmol, $RhCl(PPh_3)_3$ based on styrene, KO^{t}Bu based on styrene, 80 bar, 70 °C, 2 h.
[b] By-product: ethylbenzene; no unsaturated adduct.

Table 2 Effect of IL on the hydrosilylation reaction of styrene with triethoxysilane[a]

Entry	Catalyst	$scCO_2$/IL	Conv. (%)	Selectivity (%) β	Selectivity (%) α	TON[b]
1	$RhCl(PPh_3)_3$–KO^{t}Bu	$scCO_2$/$BMImPF_6$	91.3	85.8	14.2	1826
2		$scCO_2$/$HMImPF_6$	89.1	89.2	10.8	1782
3		$scCO_2$/$OMImPF_6$	85.4	92.3	7.7	1708
4		$scCO_2$/$OEImPF_6$	82.1	96.1	3.9	1642
5		$scCO_2$/$OBImPF_6$	75.8	98.7	1.3	1516
6[c]		$scCO_2$/$BMImPF_6$	87.3	86.1	13.9	1746
7[d]		$scCO_2$/$BMImPF_6$	81.2	86.7	13.3	1624
8[e]		$scCO_2$/$BMImPF_6$	78.5	87.2	12.8	1570
9	$[RhCl(COD)]_2$–KO^{t}Bu	$scCO_2$/$BMImPF_6$	73.9	62.0	38.0	1478
10		$scCO_2$/$HMImPF_6$	68.2	70.1	29.9	1364
11		$scCO_2$/$OMImPF_6$	63.1	76.3	23.7	1262
12		$scCO_2$/$OEImPF_6$	58.8	81.5	18.5	1170
13		$scCO_2$/$OBImPF_6$	50.3	86.7	13.3	1006

[a] Reaction conditions: styrene 30 mmol, triethoxysilane 36 mmol, $RhCl(PPh_3)_3$ 0.05 mol% based on styrene, KO^{t}Bu 0.05 mol% based on styrene, $[RhCl(COD)]_2$ 0.025 mol% based on styrene, IL 2 mL, 80 bar, 70 °C, 2 h. No by-product: unsaturated-adduct and ethylbenzene. [b] Based on Rh. [c] Second run. [d] Third run. [e] Fourth run.

Table 3 The effect of temperature on the hydrosilylation reaction of styrene with triethoxysilane[a]

Entry	$scCO_2$/IL	Temperature/°C	Conversion (%)	Selectivity (%) β	Selectivity (%) α	TON
1	$scCO_2$/$BMImPF_6$	50	44.1	89.1	10.9	882
2		70	91.3	85.8	14.2	1826
3		90	100	78.0	22.0	2000
4		110	100	70.3	29.7	2000
5	$scCO_2$/$HMImPF_6$	70	89.1	89.2	10.8	1782
6		90	100	81.1	18.9	2000

[a] Reaction conditions: styrene 30 mmol, triethoxysilane 36 mmol, $RhCl(PPh_3)_3$ 0.05 mol% based on styrene, KO^{t}Bu 0.05 mol% based on styrene, IL 2 mL, 80 bar, 2 h. No by-product: unsaturated-adduct and ethylbenzene.

Table 4 Results of the hydrosilylation reaction of other alkenes with triethoxysilane[a]

Entry	Alkene	Silane	Solvent	Conversion (%)	Selectivity (%) β	Selectivity (%) α	Selectivity (%) By-product	TON
1	1-Hexene	Triethoxysilane	$scCO_2$/$BMImPF_6$	100	100	—	—	10000
2			$scCO_2$/$HMImPF_6$	100	100	—	—	10000
3			$scCO_2$/$OMImPF_6$	100	100	—	—	10000
4			$scCO_2$/$OEImPF_6$	~ 100	100	—	—	~ 10000
5			$scCO_2$/$OBImPF_6$	99.9	100	—	—	9990
6	1-Heptene		$scCO_2$/$BMImPF_6$	100	100	—	—	10000
7	1-Octene		$scCO_2$/$BMImPF_6$	~ 100	100	—	—	~ 10000
8	1-Dodecene		$scCO_2$/$BMImPF_6$	99.9	100	—	—	9990
9[b]	2-Methyl-styrene		$scCO_2$/$BMImPF_6$	89.8	87.7	12.3	—	1796
10[b]	4-Methyl-styrene		$scCO_2$/$BMImPF_6$	93.7	82.6	17.4	—	1874
11[b]	4-Methoxy-styrene		$scCO_2$/$BMImPF_6$	95.8	79.5	20.5	—	1916
12[b]	4-Fluoro-styrene		$scCO_2$/$BMImPF_6$	94.1	90.1	9.9	—	1882
13[b]	4-Chloro-styrene		$scCO_2$/$BMImPF_6$	93.6	89.6	10.4	—	1872
14[c]	Styrene	Triethylsilane	$scCO_2$/$BMImPF_6$	100	67.6	2.7	29.7	2000

[a] Reaction conditions: alkene 30 mmol, triethoxysilane 36 mmol, $RhCl(PPh_3)_3$ 0.01 mol% based on styrene, KO^{t}Bu 0.01 mol% of styrene, IL 2 mL, 80 bar, 70 °C, 2 h. [b] Reaction conditions: styrene 30 mmol, triethoxysilane 36 mmol, $RhCl(PPh_3)_3$ 0.05 mol% based on styrene, KO^{t}Bu 0.05 mol% of styrene, IL 2 mL, 80 bar, 70 °C, 2 h. [c] Reaction conditions: styrene 30 mmol, triethylsilane 36 mmol, $RhCl(PPh_3)_3$ 0.05 mol% based on styrene, KO^{t}Bu 0.05 mol% of styrene, IL 2 mL, 80 bar, 70 °C, 2 h. By-product: unsaturated adduct, no alkane.

($HMImPF_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ($OMImPF_6$), 1-octyl-3-ethylimidazolium hexafluorophosphate ($OEImPF_6$), 1-octyl-3-butylimidazolium hexafluorophosphate ($OBImPF_6$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) were prepared as previously described.[20]

Gas chromatography (GC): TRACE DSQ GC, column DB-5 30 m × 2.5 mm × 0.25 μm, split 50 : 1, flow rate 1 mL min^{-1} constant flow, inlet temperature 260 °C, column temperature 50 °C for 1 min then 15 °C min^{-1} increase to 260 °C (held for 10 min).

^{1}H and ^{13}C NMR spectra were measured using a Bruker AV400 MHz spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts for ^{1}H and ^{13}C NMR spectra were recorded (in ppm) relative to the residual proton of $CDCl_3$. ^{1}H NMR δ 7.24; ^{13}C NMR δ 77.0.

3.2 Hydrosilylation of alkylene with triethoxysilane

A typical hydrosilylation reaction procedure was as follows: IL, catalyst, styrene and triethoxysilane were charged into a 100 cm^3 stainless steel autoclave reactor (high pressure chemical reactor; HPR-series, Supercritical Fluid Technologies, Inc.). A high pressure pump was used to introduce CO_2 into the reactor, which was maintained at the desired temperature. The reaction in CO_2 took place with stirring (about 500 rpm) for 2 h. After the reaction, the reactor was cooled to room temperature and the pressure released slowly. The product phase was separated from the catalyst by $scCO_2$, and the conversion of alkene and selectivity determined by GC analysis. The catalyst was recharged with fresh alkene and silane, and the crude product purified by distillation. All data in the tables are the average values of three experiments (Scheme 1).

Analysis of the products of the hydrosilylation reaction of styrene with triethoxysilane[21]

β-Adduct [triethoxy(phenylethyl)silane]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.00 (t, J = 8 Hz, 2H, Si–CH_2), 1.24 (t, J = 8 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).

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).

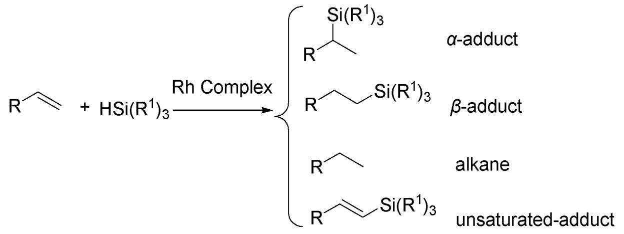
Ethylbenzene. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.15 (t, J = 8 Hz, 3H, CH_3), 2.64 (q, J = 8 Hz, 2H, CH_2), 7.11–7.25 (m, 5H, Ph).

Hydrosilylation reaction of 1-hexene with triethoxysilane

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).

Hydrosilylation reaction of styrene with triethylsilane

β-Adduct [triethyl(phenylethyl)silane]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.66 (q, J = 8 Hz, 6H, Si–CH_2), 0.92 (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).



Scheme 1 The hydrosilylation of alkenes with triethoxysilane or triethylsilane catalyzed by rhodium complexes.

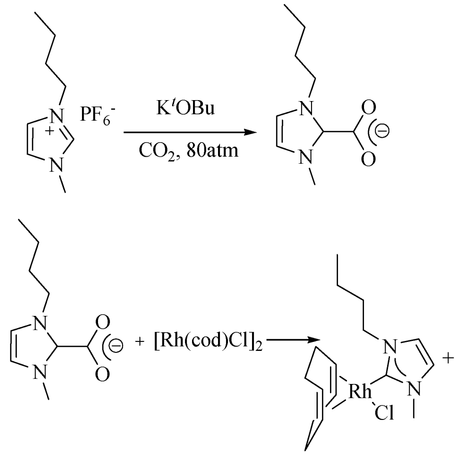
α-Adduct [triethyl(1-phenylethyl)silane]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.69 (q, J = 8 Hz, 6H, Si–CH_2), 0.97 (t, J = 8 Hz, 9H, CH_3), 1.21 (d, J = 9 Hz, 3H, CH_3), 3.58 (q, J = 8 Hz, 6H, O–CH_2), 7.15–7.23 (m, 5H, Ph).

Unsaturated adduct [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).

3.3 Synthesis of the rhodium *N*-heterocyclic carbine complex

Synthesis of 1-methyl-3-butylimidazolium-2-carboxylate. A mixture of 10.23 g (0.036 mol) of 1-methyl-3-butylimidazolium hexafluorophosphate, 4.03 g (0.036 mol) of K^{t}OBu and 30 mL of dry dimethylformamide was placed into a stainless steel autoclave fitted with a stirrer (Scheme 2). The autoclave was closed and pressurised by the introduction of CO_2 to 80 bars (1 bar = 0.1 MPa). The mixture was heated to 100 °C and kept at that temperature for 12 h. The reaction was stopped, the reactor cooled and the CO_2 released. The reaction mixture was filtered and transferred into a 100 mL tube at room temperature. After evaporation of the solvent under reduced pressure and recrystallization from CH_3CN, 4.59 g (70% yield) of a light yellow solid was obtained and characterized as 1-methyl-3-butylimidazolium-2-carboxylate. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.96 (t, J = 8 Hz, 3H, CH_3), 1.39 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 4.16 (s, 3H, N–CH_3), 4.34 (t, J = 8 Hz, 2H, N–CH_2), 7.59 (br s, 1H, Im), 7.74 (br s, 1H, Im)

Chloro(1,5-cyclooctadiene)(1-butyl-3-methylimidazole-2-ylidene)-rhodium (I). This compound was prepared by stirring a mixture of 500 mg (1.01 mmol) of bis(1,5-cyclooctadiene) dichlorodirhodium and 404 mg (2.2 mmol) of 1-methyl-3-butylimidazolium-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 dichloromethane (2 mL) and purified by repeated recrystallization from diethyl ether to give 683 mg (88% yield) of a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.81 (d, J = 4 Hz, 2H), 5.01 (m, 2H, COD CH), 4.49 (m, 2H, N–CH_2), 4.07 (s, 3H, N–CH_3), 3.34 (br s, 1H, COD CH), 3.25 (br s, 1H,



Scheme 2 Synthesis of the *N*-heterocyclic carbene–rhodium complex.

COD CH), 2.38 (m, 4H, COD CH_2), 1.98 (br m, 6H, 4H COD CH_2 and 2H Bu CH_2), 1.47 (m, 2H, Bu CH_2), 1.04 (t, J = 8 Hz, 3H, CH_3); ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 13.79, 18.42, 28.55, 32.58, 33.01, 37.73, 50.47, 58.40, 67.23 (d, $^1J_{Rh-C}$ = 14 Hz), 98.25 (d, $^1J_{Rh-C}$ = 7 Hz), 120.13, 121.95, 181.78 (d, $^1J_{C-Rh}$ = 50 Hz). These data are consistent with those reported in the literature.[18] 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%.

4. Conclusion

In summary, during the hydrosilylation of styrene with triethoxysilane in a $scCO_2$/IL system, $Rh(PPh_3)_3Cl$ had a high level of catalytic activity and selectivity for the β-adduct. When KO^tBu was added, no by-product was detected in the $scCO_2/BMImPF_6$ system. It is possible that a rhodium *N*-heterocyclic carbine complex was formed in the hydrosilylation reaction, with the PPh_3 being thought to improve the catalytic activity and selectivity of the rhodium complex. The rhodium complex was insoluble in $scCO_2$ but soluble in the ILs. The reactants and products were soluble in ILs under these reaction conditions, whereas they were resident in the $scCO_2$ phase before and after the reaction; therefore, the catalyst/IL can be reused. The substituents attached to the *N*,*N*-dialkylimidazolium cation had a strong impact on the catalytic process; the selectivity for the β-adduct clearly increased with increasing length of the alkyl chain attached to the *N*,*N*-dialkylimidazolium cation.

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