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Ni ion-containing ionic liquid salt and Ni ion-containing immobilized ionic liquid on silica: Application to Suzuki cross-coupling reactions between chloroarenes and arylboronic acids

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Abstract

Bis(1-*n*-butyl-3-methyl-imidazolium)tetrachloronickelate ($[\mathrm{Bmim}]_2[\mathrm{NiCl}_4]$), which is a nickel ion-containing ionic liquid, and immobilized nickel ion-containing ionic liquid (ImmNi^{2+}_IL) on silica surface were prepared and applied as new catalysts for Suzuki cross-coupling reactions between aryl chlorides and arylboronic acids. It was found that pretreatment of the catalysts and the addition of triphenylphosphine to the reaction system greatly promoted the reactions. Before the addition of substrates, $[\mathrm{Bmim}]_2[\mathrm{NiCl}_4]$ should be treated with K_3PO_4 in dioxane at a refluxing temperature for 1 h, and ImmNi^{2+}_IL should be treated with $\mathrm{NaO^tBu}$ in dioxane at room temperature for 30 min. An active precursor for the catalytic reactions was found to be a Ni carbene species formed by pretreatment with the bases as characterized by NMR and EXAFS. Reusability was confirmed for ImmNi^{2+}_IL.

Keywords: Ionic liquid; Suzuki cross-coupling reaction; Chloroarene; Immobilization; Ni; Phenylboronic acid; EXAFS

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1. Introduction

The nonaqueous polar property of ionic liquids makes them promising alternative solvents to traditional organic solvents and water as an immobilizing phase for transition metal catalysts in homogeneous or biphasic systems, in addition to other versatile functionalities such as electrolytes in electrochemistry and eco-friendly nonvolatile solvent in organic synthesis [1–7]. The completely ionic nature of ionic liquids makes them useful as solvents for highly charged complexes, and the low vapor pressure of ionic liquids makes it possible to use them in vacuum and as "green" solvents in industrial processes [8]. They are also considered new precursor materials for catalysts [9–12]. Dialkylimidazolium and *N*-alkyl pyridinium or quaternary ammonium-based salts are typical ionic liquids studied widely because of their ease of synthesis.

Metal ion-containing ionic liquids find various applications to catalysts, but there have been few syntheses and structure analyses of ionic liquids involving metal ions. In many cases, the properties of metal ion-containing ionic liquids were studied with samples prepared by mixing chlorine- or bromine-based ionic liquids with metal chlorides or bromides in various molar ratios. However, ionic liquids prepared by this method are usually mixtures containing several types of anionic species. It is well known that ionic liquids have the tendency to form relatively stable supercooled states, especially in the presence of impurities, indicating the need for careful handling and treatment during syntheses and measurements.

To obtain definite information on the composition, structure, and physicochemical properties of ionic liquids, it is very important to prepare pure ionic liquids with single and clear compositions. Based on these research interests, we prepared

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a series of metal ion-containing ionic liquids and characterized their structures by X-ray single crystal structure analysis and thermal and spectroscopic methods [11]. A series of metal ion-containing ionic liquids $[\mathrm{Bmim}]_2[\mathrm{MCl}_4]$ (M = Sn, Cu, Ni, Mn, Fe, Co, Zn, and Pt) and $[\mathrm{Bmim}]_2[\mathrm{ZrCl}_6]$ were synthesized and single crystal structures were determined. The melting point of the synthesized salts and the degree of the local symmetry of metal chloride anions were found to be closely correlated with each other. Ionic conductivity was measured for supercooled states of the synthesized salts and it was found that these salts behaved as ionic liquids unambiguously. Moreover, the metal ion-containing ionic liquids were covalently immobilized on silica surface (Imm_IL) and characterized by EXAFS and DR UV/vis [12]. It was found that Cu^{2+}-containing ionic liquid (ImmCu^{2+}_IL) gave high activities for Kharasch addition reactions [12]. There are previous reports on immobilization of ionic liquids involving FeCl_3, SnCl_2, and AlCl_3 [13–17]. Valkenberg et al. [13,16] introduced the term “novel Lewis acid catalysts” (NLACs) in the immobilization of ionic liquids; our method [12] for immobilization can be classified as NLAC II (immobilization via cation).

In this study we focus on Ni-catalyzed Suzuki cross-coupling reactions using Ni ion-containing ionic liquid and Ni ion-containing immobilized ionic liquid on silica surface as an extension of our study [11,12]. The Suzuki cross-coupling reaction [18,19] between arylboronic acids and aryl halides or triflates is one of the most important methods for synthesizing biaryls, which are useful for natural products, polymers, advanced materials, and target molecules of medicinal chemistry. In ionic liquid media, a Pd-catalyzed Suzuki cross-coupling reaction has been reported for bromoarenes [20] in a homogeneous system and for iodoarenes immobilized on a resin [21]. Although palladium-catalyzed Suzuki coupling reactions can achieve high yields when aryl bromides, iodides, and triflates are used, chloroarenes, which are economical and easily available substrates, have been used only rarely, because the oxidation addition of chloroarenes to palladium(0) is too slow to allow development of the catalytic cycle. Recently several research groups solved this problem with Pd. The application of stable carbene, imidazol-2-ylidene, to palladium-catalyzed Suzuki coupling reactions [22–24] makes the Pd catalysts active to chloroarenes. Layered double hydroxide-supported nanopalladium catalyst [25] has been reported to be active to chloroarenes. Recently, hydroxyapatite-bound palladium complex was reported to catalyze the Suzuki cross-coupling reaction with chloroarene in the presence of TBAB [26]. Nickel catalysts, which are much cheaper than precious metals like palladium, have been reported to be active for the Suzuki reactions of chloroarenes in the presence of four equivalents of phosphine ligands [27–32]. However, these systems suffer from problems involved with using strong reducing agents, a large amount of catalyst (up to 10 mol%), expensive phosphine ligands, and prolonged reaction times, which do not favor practical large-scale use. These issues are awaiting resolution by newly designed economically feasible catalysts.

In this work we present for the first time the catalytic applications of Ni^{2+}-containing ionic liquid ($[\mathrm{Bmim}]_2[\mathrm{NiCl}_4]$) and immobilized ionic liquid (ImmNi^{2+}_IL) to the Suzuki cross-coupling reactions between chloroarenes and arylboronic acids.

2. Experimental

2.1. Materials

Anhydrous 1-methylimidazole (>99%) and 3-trimethoxysilylpropyl chloride (>97%), o-tolylboronic acid, 2,6-dimethylphenylboronic acid, 3-thiopheneboronic acid, and anhydrous potassium phosphate (97%) were purchased from Aldrich. Anhydrous NiCl_2 (99.9%), 1-chlorobutane (98.0%), and all other chemicals were purchased from WAKO. $\mathrm{K}_3\mathrm{PO}_4$ was crushed into a fine powder and dried under vacuum at 413 K for 2 h before use. All dehydrated solvents stored under nitrogen atmosphere were purchased from WAKO and used without further purification except 1,4-dioxane, which was dehydrated again before use with metal sodium and stored under nitrogen atmosphere. Aerosil 300 (surface area 300 m^2/g), supplied by Japan Aerosil Co., use as support. The calcined support was kept in dry nitrogen.

2.2. X-ray fluorescence

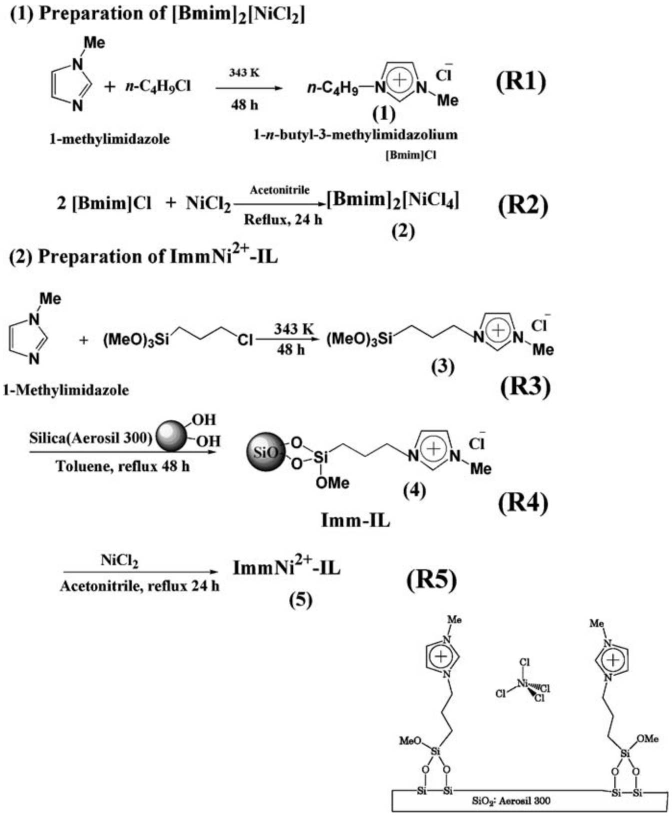
X-ray fluorescence analysis (XRF) was done using a SEA-2010 spectrometer (Seiko Electronic Industrial Co.). Physical mixtures of metal chloride salts and support Aerosil 300 in various ratios were used to make calibration lines to estimate the metal loadings in immobilized ionic liquids.

2.3. EXAFS measurements

Measurements of extended X-ray absorption fine structure (EXAFS) at the Ni K-edge were carried out at the Photon Factory in the Institute of Materials Structure Science, High-Energy Accelerator Research Organization (KEK-MSS-PF). The measurements were made in a transmission mode at BL-12C at room temperature. Synchrotron radiation from the storage ring was monochromatized by a Si(111) channel-cut crystal. Ionization chambers used as detectors for incident X-ray (I_0) and transmitted ray (I) were filled with $\mathrm{Ar/N_2}$ mixture (1:1) gas and Ar gas, respectively. The samples were handled in dry nitrogen. The EXAFS raw data were analyzed with the UWXAFS analysis package [33], including the background subtraction program AUTOBK [34] and the curve-fitting program FEFFIT [35]. Backscattering amplitudes and phase shifts were calculated using FEFF8.0 [36].

2.4. Catalyst preparation

The catalyst preparation procedures are summarized in Scheme 1 [11,12]. All processes were conducted under nitrogen atmosphere. 1-n-Butyl-3-methylimidazolium chloride ([Bmim]Cl, **1**) was obtained by refluxing a mixture of N-methylimidazole and 1-chlorobutane (**R1**). Purification of the obtained product was achieved by recrystallization. Bis(1-n-butyl-3-methylimidazolium) tetrachloronickelate(II) ($[\mathrm{Bmim}]_2$



Scheme 1. Preparation steps for $[Bmim]_2[NiCl_4]$ and $ImmNi^{2+}$_IL.

$[NiCl_4]$, **2**) was obtained by refluxing the compound **1** and anhydrous nickel(II) chloride dissolved in dry acetonitrile (**R2**), then recrystallizing from acetonitrile solution.

For the preparation of immobilized ionic liquid catalysts, 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (**3**) was synthesized by refluxing the mixture of N-methylimidazole and 3-trimethoxysilylpropyl chloride (**R3**).

In a glovebox, pretreated Aerosil 300 and the compound (**3**) (weight ratio 1:1) were dispersed in dehydrated toluene in a Schlenk tube, and the mixture was refluxed for 48 h in nitrogen (**R4**). Toluene was removed under reduced pressure, and the resulting material was transferred to a Soxhlet tube in nitrogen. The excess ionic liquid was removed by Soxhlet extraction with dichloromethane. The resulting solid is denoted as Imm_IL (**4**). Elemental analysis was performed for this sample. Anal. found: C, 7.36; H, 1.92; N, 1.54. The density of immobilized ionic liquid functional groups was estimated as ca. 1.2 nm^2 based on the nitrogen percentage in the elemental analysis. Note that no N-containing solvent was used for the preparation of Imm_IL.

In the next step, Imm_IL was added to an acetonitrile solution of $NiCl_2$ in a 50-ml Schlenk tube and refluxed for 24 h (**R5**). Acetonitrile was removed at a reduced pressure, and excess $NiCl_2$ was removed by Soxhlet extraction with acetonitrile for 48 h. The prepared immobilized ionic liquid is denoted as $ImmNi^{2+}$_IL (**5**). The Ni loading was determined by XRF to be 3.3 wt%. The amount of $NiCl_2$ was calculated as 0.6 Ni ion nm^{-2}.

2.5. Catalytic reactions

All experiments were carried out under nitrogen atmosphere using standard Schlenk techniques. The yields were referred to gas chromatography (GC) yields based on chloroarenes. The products were analyzed with a Shimadzu gas chromatograph (GC-14B) with a flame ionization detector using a 30 m × 0.25 mm NEUTRA Bond-1 column. GC-mass spectroscopy (MS) measurements were performed on Shimadzu GCMS-QP5000 for assigning GC peaks.

$[Bmim]_2[NiCl_4]$-catalyzed Suzuki reactions without pretreatment were examined by mixing $[Bmim]_2[NiCl_4]$ (0.02 mmol), K_3PO_4 (0.85 g, 4 mmol), phosphine, chloroarene (2 mmol), arylboronic acid (2.4 mmol), and solvent in a 50-ml Schlenk tube and stirring at 353 K for a prespecified time. It was found that the reaction without any pretreatment resulted in very low activity; consequently, a way of pretreating the catalysts to promote the reaction was sought. $[Bmim]_2[NiCl_4]$ (0.02 mmol) and K_3PO_4 (0.85 g, 4 mmol) were mixed in a 50-ml Schlenk tube, to which solvent was added, and the mixture was refluxed for 1 h. After the pretreatment, phosphine, chloroarene (2 mmol), and arylboronic acid (2.4 mmol) were added, and the vessel was sealed with a septum wrapped with wire. The mixture was stirred at 353 K for a prespecified time.

Immobilized catalysts were also used for the Suzuki reactions with various pretreatment methods. $ImmNi^{2+}$_IL (0.04 mmol) and K_3PO_4 (0.85 g, 4 mmol) or NaO^tBu (0.16 mmol, 16 mg) were mixed in a 50-ml Schlenk tube, after which the solvent was added and the mixture was stirred at refluxing temperature (in the case of K_3PO_4) or room temperature (in the case of NaO^tBu) for a prespecified time. After the pretreatment, phosphine, chloroarene (2 mmol), and arylboronic acid (2.4 mmol) were added, and the vessel was sealed with a septum wrapped with a wire.

3. Results and discussion

3.1. EXAFS analysis for $ImmNi^{2+}$_IL

The crystal structures of $[Bmim]_2[NiCl_4]$ has been determined by X-ray single crystal structure analysis, which will be reported separately [11]. $[Bmim]_2[NiCl_4]$ crystallizes in space group Cc of a monoclinic structure with $a = 9.450(1)$ Å, $b = 16.410(1)$ Å, $c = 15.439(2)$ Å, $\beta = 104.946(2)°$, and $Z = 4$. Its asymmetric unit (Fig. 1) contains two $[Bmim]^+$ cations and one $[NiCl_4]^{2-}$ anion. The two butyl chains on the two imidazolium rings cross each other at nearly right angles. The anion $[NiCl_4]^{2-}$ has a distorted tetrahedron, and the mean angle of Cl–Ni–Cl is 115.8°. The mean Ni–Cl bond length of $[NiCl_4]^{2-}$ is 2.249 Å.

The $ImmNi^{2+}$_IL was characterized by Ni K-edge EXAFS. To determine the coordination number (CN) around Ni, the amplitude reduction factor S_0^2 should be determined using a reference compound with a known structure. The structure of ionic liquid $[Bmim]_2[NiCl_4]$ has already been determined as mentioned above, which has a coordination number of 4; thus $[Bmim]_2[NiCl_4]$ was used as a reference compound

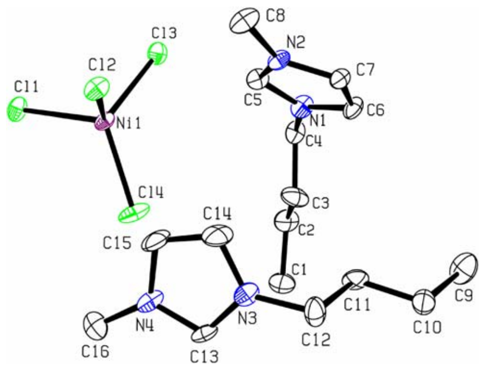
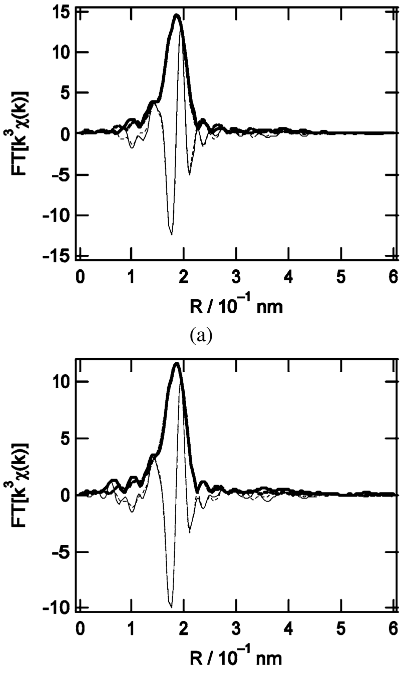


Fig. 1. The ORTEP drawing of the asymmetric unit of $[Bmim]_2[NiCl_4]$ at the 50% probability level. Hydrogen atoms are omitted for clarity.



(a)

(b)

Fig. 2. k^3-Weighted Fourier transform (amplitude (thick curve) and imaginary part (thin curve)) of Ni K-edge EXAFS. (a) $[Bmim]_2[NiCl_4]$ and (b) $ImmNi^{2+}$_IL (3.3 wt% Ni). Observed data: solid curves; fitting data: dotted curves.

for determining the local structure of $ImmNi^{2+}$_IL. The k^3-weighted EXAFS Fourier transform for $[Bmim]_2[NiCl_4]$ is shown in Fig. 2a. The parameter S_0^2 was determined to be 0.83 by curve-fitting the experimental EXAFS function, in which the coordination number was fixed at 4. Then the obtained S_0^2 (0.83) was used in curve-fitting the EXAFS data for $ImmNi^{2+}$_IL. The structural parameters for the reference compound $[Bmim]_2[NiCl_4]$ and $ImmNi^{2+}$_IL are summarized in Table 1. The k^3-weighted EXAFS Fourier transform for $ImmNi^{2+}$_IL is shown in Fig. 2b. Within the fitting uncertainty, the distance and coordination number of Ni–Cl bond in $ImmNi^{2+}$_IL are the same as those in $[Bmim]_2[NiCl_4]$, indicating that the local structure around the Ni ion in $ImmNi^{2+}$_IL is almost the same as that in $[Bmim]_2[NiCl_4]$. The schematic view of $ImmNi^{2+}$_IL is shown at the bottom of Scheme 1, with the nickel ion held between two imidazolium ions.

3.2. Suzuki cross-coupling reactions with the ionic liquid $[Bmim]_2[NiCl_4]$

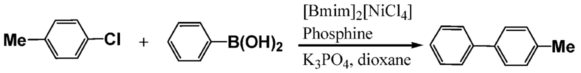
When $[Bmim]_2[NiCl_4]$ was used as a catalyst for the Suzuki coupling reaction without any treatment, the yield was quite low. Grasa et al. [22] and McLachlan et al. [37] have shown that Pd/imidazolium catalysts should be pretreated before substrates are added, to obtain a catalytically active solution. In our initial study, the pretreatment of $[Bmim]_2[NiCl_4]$ with K_3PO_4 in dioxane at a refluxing temperature for 1 h greatly improved catalyst activity; the catalyst seemed to change into a different chemical species. Various bases were used for the pretreatment, and anhydrous K_3PO_4 was found to be the best base for performance. Indeed, anhydrous K_3PO_4 has been most widely used in nickel-catalyzed Suzuki reactions in dioxane [27–31,38]. Based on the above information, the reaction conditions were optimized using anhydrous K_3PO_4 as base and dioxane as solvent, whereas the pretreatment of $[Bmim]_2[NiCl_4]$ with K_3PO_4 at refluxing temperature for 1 h before the addition of arylchloride and arylboronic acid was carried out in dioxane (Table 2).

It is known that nickel phosphine complexes are active for the Suzuki cross-coupling of chloroarenes in the existence of additional phosphine ligands. Although in the absence of any phosphines, $[Bmim]_2[NiCl_4]$ was active for the substrates of iodoarenes and bromoarenes, it gave a low yield of 23% for 4-chlorotoluene (Table 2, entry 1). To improve the activity, the effect of phosphines on the yield was investigated (entries 2–10). The addition of PPh_3 in various equivalents with respect to nickel produced a great increase in yield upon the increment of the equivalent of PPh_3, with yield reaching 96% at the equivalent of 2 (entry 6). Increasing the amount of PPh_3 over 3 equivalents had no further effect on yield (entry 7; see also Fig. 3a). The effects of different phosphines in two equivalents were also investigated (entries 8–10; Fig. 3b). Dppf, the most widely used ligand in Ni catalytic systems, gave a yield of only 15%. Dppf's low activity might be due to its bulky steric effect, which is incompatible with ligands from ionic liquid. For this reason, PPh_3, the most common, inexpensive, and stable phosphine, was the best choice. Under the same conditions as those for entry 6, however, a Ni-phosphine complex $NiCl_2(PPh_3)_2$ gave a yield of 10% (entry 18). Although $[Bmim]_2[NiCl_4]$ without PPh_3 was a little more active (yield 23%) than $NiCl_2(PPh_3)_2$,

Table 1
EXAFS fitting results for $[Bmim]_2[NiCl_4]$ and $ImmNi^{2+}$_IL

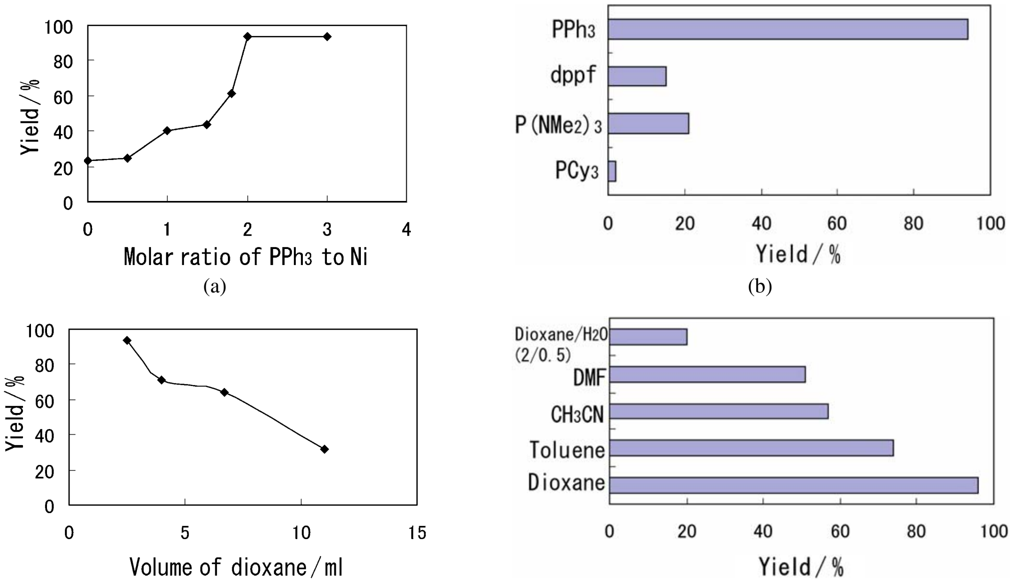
	Bond	CN	R (10^{-1} nm)	DW (10^{-5} nm^2)	Δk (10 nm^{-1})	ΔR (10^{-1} nm)	S_0^2	ΔE_0 (eV)	R_f (%)
$[Bmim]_2[NiCl_4]$	Ni–Cl	4.00	2.267 ± 0.003	4.6 ± 0.3	3.0–13.0	1.0–3.0	0.83 ± 0.04	1.6 ± 0.6	0.53
$ImmNi^{2+}$_IL	Ni–Cl	3.6 ± 0.2	2.268 ± 0.003	6.1 ± 0.4	3.0–13.0	1.0–3.0	0.83	2.1 ± 0.6	0.65

Table 2
Optimization of reaction conditions for the Suzuki cross coupling reaction between 4-chlorotoluene and phenylboronic acid on the $[Bmim]_2[NiCl_4]$ catalyst[a]



Entry	Phosphine[a]	Solvent[b]	Yield (%)	Entry	Phosphine[b]	Solvent[c]	Yield (%)
1	None	Dioxane (0.63)	23	11	PPh_3 (2.0)	Dioxane (1.0)	71
2	PPh_3 (0.5)	Dioxane (0.63)	25	12	PPh_3 (2.0)	Dioxane (1.7)	64
3	PPh_3 (1.0)	Dioxane (0.63)	40	13	PPh_3 (2.0)	Dioxane (2.8)	32
4	PPh_3 (1.5)	Dioxane (0.63)	44	14	PPh_3 (2.0)	Toluene (0.63)	74
5	PPh_3 (1.8)	Dioxane (0.63)	61	15	PPh_3 (2.0)	Acetonitrile (0.63)	57
6	PPh_3 (2.0)	Dioxane (0.63)	96	16	PPh_3 (2.0)	DMF (0.63)	51
7	PPh_3 (3.0)	Dioxane (0.63)	94	17	PPh_3 (2.0)	Dioxane/H_2O (0.5/0.13)	20
8	PCy_3 (2.0)	Dioxane (0.63)	2	18	$NiCl_2$ $(PPh_3)_2$[d]	Dioxane (0.63)	10
9	$P(NMe_2)_3$ (2.0)	Dioxane (0.63)	21	19	PPh_3 (2.0)[e]	Dioxane (0.63)	64
10	Dppf (2.0)	Dioxane (0.63)	15				

[a] Reaction conditions: $[Bmim]_2[NiCl_4]$, 0.04 mmol (1.0 mol%); 4-chlorotoluene, 4 mmol; phenylboronic acid, 4.8 mmol; K_3PO_4, 8 mmol; 353 K; 20 h.
[b] The amount of phosphine was expressed as the molar ratio with respect to Ni.
[c] The amount of solvent was expressed as the volume (ml) with respect to 1 mmol of chlorotoluene.
[d] 1 mol% was used.
[e] No pretreatment was done.



(a) (b)

(c) (d)

Fig. 3. Summary of reaction conditions for the Suzuki coupling reaction catalyzed by $[Bmim]_2[NiCl_4]$. (a) Effect of molar ratio of PPh_3 to Ni, (b) effect of phosphines, (c) effect of volume of dioxane, (d) effect of solvent.

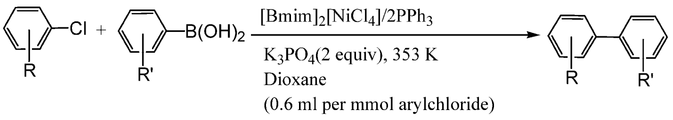
$[Bmim]_2[NiCl_4]$ in the presence of 2 equivalents of PPh_3 ligands showed the highest activity (yield 96%, entry 6).

No studies on the effect of solvent volume have been reported to date. When the ratio of dioxane increased from ca. 0.6 to 1.0 ml per mmol of chlorotoluene, the yield decreased to 71% (entry 11); at ca. 2.8 ml per mmol of chlorotoluene, the yield decreased dramatically, to 32% (entry 13; Fig. 3c). The effects of other solvents at the ideal ratio of 0.63 ml per mmol of chlorotoluene are reported in Table 3 (entries 14–16) and Fig. 3d. The lower yield in toluene (74%) might be due to the low solubility of K_3PO_4 in the less polar solvent. Although K_3PO_4 has greater solubility in acetonitrile and DMF than in toluene and dioxane, the coordinating properties of DMF and acetonitrile may cause a poisoning effect on the catalyst. Adding water to the dioxane also resulted in a low yield of 20% (entry 17). The ratio of 0.6 ml per mmol of chlorotoluene is necessary to keep the reaction system in good stirring state.

The time dependence of the yield under the optimized condition is shown in Fig. 4. There was an induction period of about 7 min during which the catalyst was reduced to Ni(0), the active species in the Suzuki reaction. The turnover frequency (TOF) for the Suzuki cross-coupling reaction between chlorotoluene and phenylboronic acid was calculated as 255 h^{-1}—to the best of our knowledge, the highest value yet reported for Ni catalysts.

The cross-coupling reactions between several substituted arylboronic acids and aryl chlorides were performed in a standard set of reaction conditions. As shown in Table 3,

Table 3
$[Bmim]_2[NiCl_4]/PPh_3$ catalyzed Suzuki cross coupling reactions[a]



Entry	*R*	*R*[b]	Catalyst (mol% Ni)[c]	Time (h)[d]	Yield (%)[e]
1	4-CH_3CO–		0.5	2	100
2	4-CN–		0.5	2	100
3	4-CHO–		1.0	2	87
4	4-CF_3–		0.5	2	100
5	4-(PhCO)–		0.5	2	100
6	4-CH_3–		0.5	20	96
7	4-CH_3O–		1.0	20	94
8	4-CH_3OOC–		1.0	18	83
9	2-CH_3–		1.0	18	90
10	2-CH_3– 6-CH_3–		1.0	24	37
11	4-CH_3–	2-CH_3–	1.0	18	83
12	4-CH_3–	2-CH_3– 6-CH_3–	1.0	18	0
13	4-CH_3–	3-thiopheneboronic acid	1.0	18	19

[a] Pretreatment was conducted by refluxing the mixture of $[Bmim]_2[NiCl_4]$ and K_3PO_4 in dioxane for 1 h, and then PPh_3, substrate and arylboronic acid were added to start the reaction. Reaction conditions: $PPh_3/Ni = 2$; 3.0 mmol aryl chlorides; 3.6 mmol arylboronic acid; 6.0 mmol K_3PO_4. Reactions were carried out at 353 K under nitrogen atmosphere.

[b] Vacancy represents no specific substitutional group.

[c] Catalyst mol%Ni was defined with respect to arylchloride.

[d] Reaction time was not optimized.

[e] Yield was determined by GC.

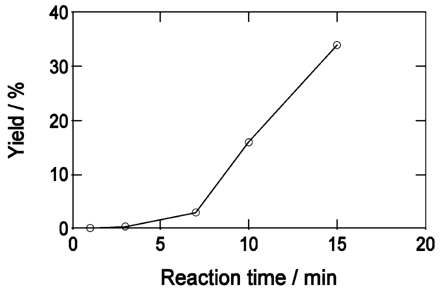


Fig. 4. Variation of yield with reaction time in the $[Bmim]_2[NiCl_4]/2PPh_3$ catalytic system at 353 K.

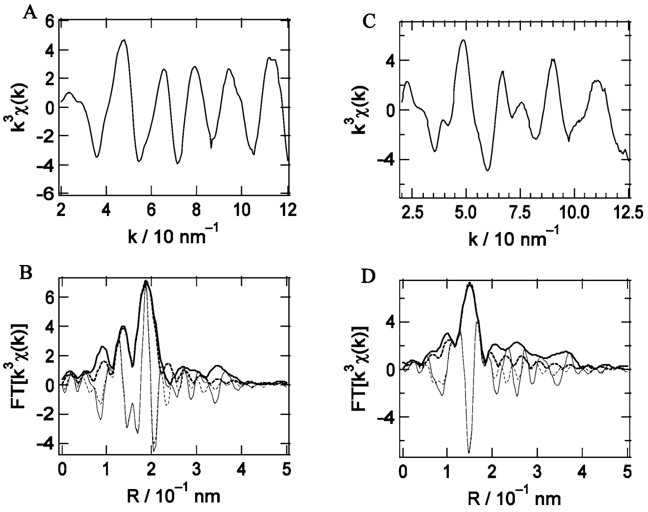


Fig. 5. Ni *K*-edge EXAFS data for the brown complex ((A) k^3-weighted EXAFS oscillation, (B) k^3-weighted Fourier transform) and the yellow complex ((C) k^3-weighted EXAFS oscillation, (D) k^3-weighted Fourier transform). Thick solid curve and thick dotted curve represent observed and fitted absolute values, respectively. Thin solid curve and thin dotted curve represent observed and fitted imaginary parts, respectively.

$[Bmim]_2[NiCl_4]/PPh_3$ was able to catalyze the Suzuki reactions for substrates with various functional groups. Chloroarenes with electron-withdrawing substituents (entries 1, 2, 4, and 5) gave 100% yields of cross-coupling products after 2 h using 0.5 mol% catalyst. The slightly lower yield for substrates with having –CHO and –COOMe (entries 3 and 8) may be due to the instability of the substituents under basic reaction conditions. Chloroarenes with an electron-donating group, such as –Me and –OMe, also gave excellent yields (>90%). Ortho-monosubstituted chloroarene readily coupled with phenylboronic acid, and vice versa (entries 9 and 11). However, ortho-dimethyl groups were not tolerated (entries 10 and 12). Arylboronic acid with heteroatoms could not readily couple with chloroarene (entry 13).

3.3. Nature of the pretreated species

The pretreated species was characterized by NMR and EXAFS. When the blue $[Bmim]_2[NiCl_4]$ was pretreated with K_3PO_4 in dioxane, a brown color complex was obtained in the first 30 min, with a yellow complex formed in the subsequent 30 min. The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the yellow complex showed a resonance from the carbene carbons at $\delta = 166.8$ ppm, which is in the range for Ni(II) carbene complex (160–170 ppm) [39–44]. The reported chemical shift of carbene carbon in Ni(0) carbene complexes ranges from 190 to 225 ppm [45,46]. The carbene complexes were also characterized with Ni *K*-edge EXAFS (brown complex, Figs. 5A and 5B; yellow complex, Figs. 5C and 5D). The fitting results are presented in Table 4. The Ni atom of the brown com-

Table 4
EXAFS curve-fitting results for the brown and yellow color complexes

Bond	Brown color complex[a]			Yellow color complex[b]		
	CN	*R* (10^{-1} nm)	DW (10^{-5} nm^2)	CN	*R* (10^{-1} nm)	DW (10^{-5} nm^2)
Ni–Cl	2 ± 1	2.22 ± 0.02	3 ± 4			
Ni–C	1.4 ± 1.3	1.88 ± 0.06	0 ± 7	4 ± 1	1.92 ± 0.02	3 ± 4

[a] $\Delta E_0 = 8 \pm 2$ eV; $\Delta k = 30$–117 nm^{-1}; $\Delta R = 0.10$–0.30 nm; $S_0^2 = 0.73$; $R_f = 4.70\%$.

[b] $\Delta E_0 = 8 \pm 3$ eV; $\Delta k = 30$–120 nm^{-1}; $\Delta R = 0.10$–0.20 nm; $S_0^2 = 0.73$; $R_f = 0.73\%$.

plex was coordinated by two chlorine atoms and two carbon atoms at distances of 0.222 and 0.188 nm, respectively. The Ni atom of the yellow complex has four nearest carbons located at 0.192 nm. These results show that the 1-h pretreatment changed $[Bmim]_2[NiCl_4]$ to a Ni(II) complex with carbene ligands corresponding to dehydrogenated imidazolium cations. Herrmann et al. also reported [44] $NiCl_2(carbene)_2$ species with a Ni–Cl distance of 0.218 nm and a Ni–C distance of 0.191 nm, corresponding to the brown complex. Douthwaite et al. [43] reported Ni(II)(carbene)$_4$ species with an average Ni–C distance of 0.193 nm, corresponding to the yellow complex in the present study.

3.4. *Suzuki cross-coupling reactions on the immobilized ionic liquid ImmNi^{2+}_IL*

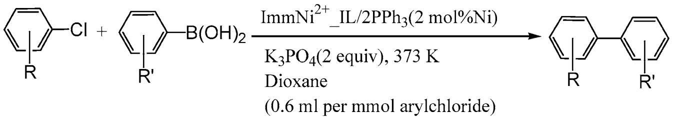
Although $[Bmim]_2[NiCl_4]/PPh_3$ showed high activity and selectivity in the Suzuki cross-coupling reactions, separating the catalyst from the reaction mixture proved difficult. The immobilized catalyst ImmNi^{2+}_IL, which can address this problem, was applied to the Suzuki cross-coupling reactions.

The effects of pretreatment and PPh_3 were examined as follows. In the absence of PPh_3, 10 h of pretreatment of ImmNi^{2+}_IL with K_3PO_4 in refluxing dioxane gave a very low yield of 2%, and 24 h of pretreatment gave a low yield of 46%. The low solubility of K_3PO_4 in the solvent and the presence of the support surface mandated a greatly prolonged time for pretreating the immobilized catalyst. However, the addition of PPh_3 had no effect on the yield, unlike the case of $[Bmim]_2[NiCl_4]$. The prolonged pretreatment may change the ionic liquid into a species that cannot interact with PPh_3. To decrease the pretreatment time, a strong base NaO^{t}Bu was applied in this system. Pretreatment with NaO^{t}Bu for 30 min at room temperature affected the reaction a little, resulting in a yield of 52%; the addition of PPh_3 further enhanced the yield to 84%. If 2 mol% of ImmNi^{2+}_IL was used, the highest yield of 94% at 373 K was obtained; however, the yield decreased to 13% at 353 K.

Under the optimized reaction conditions, the TOF of the ImmNi^{2+}_IL/PPh_3 catalytic system was determined to be 162 h^{-1} based on the yield in the first 20 min. The lower TOF value for the immobilized catalyst is ascribed to immobilization of the active sites on the support and the limited accessibility of the reactants compared with the ionic liquid catalysts. Cross-coupling reactions between several substituted arylboronic acids and aryl chlorides were conducted; the performances are given in Table 5. ImmNi^{2+}_IL/PPh_3-catalyzed Suzuki reactions were exceptionally tolerant to various functional groups on both aryl chlorides and arylboronic acids. Comparing Table 3 with Table 5 shows very similar activity patterns in catalytic systems ImmNi^{2+}_IL/PPh_3 and $[Bmim]_2[NiCl_4]/PPh_3$ for the same substrates, except for *p*-chlorobenzaldehyde, which gave a higher yield with ImmNi^{2+}_IL/PPh_3 (100%) than with $[Bmim]_2[NiCl_4]/PPh_3$ (87%) (entry 3 in both tables).

Reuse of ImmNi^{2+}_IL was examined up to the third cycle. The reuse procedure involved retrieving solid-phase including catalyst and base by filtration, followed by washing with dichloromethane, then performing the next reaction by adding 1 equivalent of base, phosphine, substrates, and solvent. In the first reuse, the yield was maintained at 94%. The reaction of the filtrate was examined after adding reactants and base, and negligible product was found, indicating that leaching of the immobilized catalyst hardly occurs. The yield was reduced to 69% on the second reuse and 64% on the third reuse, probably because the relative content of catalysts decreased. These results indicate reusability of the immobilized catalyst ImmNi^{2+}_IL.

Table 5
ImmNi^{2+}_IL/PPh_3 catalyzed Suzuki cross coupling reactions (2 mol% Ni)[a]



Entry	*R*[b]	*R′*[b]	Time (h)[c]	Yield (%)[d]
1	4-CH_3CO–		1	100
2	4-CN–		1	100
3	4-CHO–		2	100
4	4-(PhCO)–		3	90
5	4-CF_3–		5	94
6	4-CH_3OOC–		5	71
7	4-CH_3–		5	94
8	4-CH_3–		0.33	70
9	2-CH_3–		10	96
10	4-CH_3O–		7	87
11		2-CH_3–	10	95
12		2-CH_3– 6-CH_3–	20	6
13		3-thiopheneboronic acid	15	31
14	2-CH_3– 6-CH_3–		20	9

[a] Pretreatment was conducted by stirring the mixture of ImmNi^{2+}_IL and NaO^{t}Bu (4 equiv(Ni)) in dioxane at RT for 30 min. Reaction conditions: $PPh_3/Ni = 2$; 1.5 mmol aryl chlorides; 1.8 mmol arylboronic acids; 3.0 mmol K_3PO_4; 373 K; reactions were carried out under N_2.

[b] Vacancy represents no specific substitutional group.

[c] Reaction time was not optimized.

[d] Yields determined by GC.

4. Conclusion

New $[Bmim]_2[NiCl_4]$ and ImmNi^{2+}_IL were synthesized and applied as the first examples of Ni ion-containing ionic liquids and immobilized ionic liquids to Suzuki cross-coupling reactions between substrates with various functional groups. Both of the catalysts showed very high activity and selectivity for the cross-coupling reactions between aryl chlorides and arylboronic acids in the presence of 2 equivalents of PPh_3. A Ni carbene species produced by pretreating the catalysts with K_3PO_4 or NaO^{t}Bu in dioxane was suggested to be a catalytically active species for the Suzuki cross-coupling reaction as characterized by NMR and EXAFS. The reaction conditions were optimized to find the best yield of the reactions. The activity of the catalyst $[Bmim]_2[NiCl_4]$ was the highest yet reported for Ni catalysts. The ImmNi^{2+}_IL catalyst was reusable, albeit with a slightly decreased yield, whereas separating $[Bmim]_2[NiCl_4]$ from the reaction products proved very difficult.

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