N-Heterocyclic Carbene Conjugated with Poly(ethylene glycol) for Palladium-Catalyzed Suzuki–Miyaura Coupling in Aqueous Solvents

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Abstract Here we report a type of *N*-heterocyclic carbene (NHC)- and phosphine-chelated palladium catalysts with poly(ethylene glycol) (PEG) chain for Suzuki–Miyaura cross-coupling reactions. 1-(2-Diphenylphosphinoferrocenyl)-ethyl-3-imidazolium iodides conjugated with MeO–PEG₄₀₀ and MeO–PEG₇₅₀, respectively, have been synthesized and characterized. It was demonstrated that the salts bearing with PEG chain could act as NHC precursors successfully under the catalytic condition to form NHC-supported palladium complexes joined by phosphine. The formed palladium complexes are highly efficient for Suzuki–Miyaura coupling of aryl bromides with phenylboronic acid at the palladium loading of 0.1 mol% in both organic and aqueous solvents.

Keywords *N*-Heterocyclic carbene · PEG · Palladium · Suzuki–Miyaura reaction · Aqueous catalysis

1 Introduction

Since the isolation of stable free *N*-heterocyclic carbene (NHC) by Arduengo st al. [1, 2] increasing attention has

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been focused on using them as ancillary ligands for transition metals [3–8]; they are alternatives to phosphine, however, with a lower π -acceptor ability, resulting in the coordinated metal center being richer in electron density [9]. Compared to other organic ligands, the dissociation energy between transition metals and NHC ligands is higher, and consequently those complexes with NHCs have excellent stabilities to air and moisture [10, 11]. The electron-rich characteristics have been shown significantly benefits in NHC-supported transition metals, such as palladium [12–19], ruthenium [20–23], rhodium [24–26], and nickel [27–29], as catalysts for organic transformation.

Generally, homogeneous transition metal catalysis can provide best reaction condition via ligand-tuning to achieve high activities, while heterogeneous catalysis offers the advantages of a simplified product separation and the recycling of catalyst. Therefore, immobilization of homogeneous catalysts, including by organic polymers [30–33] and inorganic materials [34–36], has attracted much attention to combine both the advantages of homo- and hetero-geneous catalysis [37, 38]. In addition, intensive efforts have also been paid to reduce or eliminate the use of flammable, hazardous, and expensive organic solvents in the Green chemistry [39–42].

Catalyst leaching often occurs in immobilized homogeneous catalysts; the high dissociation energies between NHCs and many transition metals look to offer possibilities to avoid the leaching problem [43]. Merrifield and Wang resins have been successfully applied as supports for NHCtransition metal catalysts. Particularly, water-soluble transition-metal-NHC complexes for aqueous-phase catalysis have attracted more and more attentions [44–49]. Some NHC–palladium complexes have also been tethered with poly(2-oxazoline)s and poly(norborn-2-ene) for C–C bondforming reactions [50, 51]. Recently, two of poly(ethylene

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glycol) (PEG) conjugated NHC ligands have been reported and used for ruthenium-catalyzed olefin metathesis [52, 53]. The PEG-tag will make the incorporated catalyst soluble in water as well as in some of organic solvents, such as toluene and dichloromethane, however insoluble in hexane, diethyl ether, *tert*-butylmethyl ether, isopropyl alcohol, and cold ethanol, etc. The solubility character of PEG would be beneficial for the catalysis occurring in homogeneous phase in a wide range of solvents and useful for separating product from catalyst [54].



2,6-dimethylphenyl (**1f**), 2,4,6-trimethylphenyl (**1g**), 2,6-diisopropylphenyl (**1h**)

(1)

A series of 1-(2-diphenylphosphinoferrocenyl)ethyl-3-substituted-imidazolium iodides (1, Eq. 1) were prepared [55] and found to be efficient in the palladium-catalyzed Suzuki-Miyaura cross-coupling reaction (Eq 2), the catalyst Pd(OAc)₂/ 1d showing up to 20,000 turnover numbers for coupling 4-bromotoluene with phenylboronic acid [56]. The system Pd(OAc)₂/1 is also effective for Hartwig–Buchwald amination of aryl bromides and chlorides [57]. These results inspired us to prepare the water-soluble analogues of the imidazolium salts 1 for aqueous catalysis. The imidazolium salt bridged by a short PEG chain has been found to be useful as supporting ligand for palladium-catalyzed Suzuki-Miyaura reactions [58], but the solubility of the supported catalyst in water is low. Towards taking the benefits of PEG, we report here the synthesis of 1-(2diphenylphosphinoferrocenyl)ethyl-3-substituent-imidazolium iodides conjugated with different length of PEG chain and their application in the palladium-catalyzed Suzuki-Miyaura reaction in both organic and aqueous solvents.



2 Results and Discussion

2.1 Preparation of the PEG-Bound Ferrocenylphosphine–Imidazoliun Salts

Recently, it has been established that the readily available ferrocenyl derivative **2** [55, 56] reacts with 1-substituent-

imidazole to afford ferrocenylphosphine–imidazolium salts in high yields. Therefore, a target poly(ethylene glycol)bound imidazolium salt could be produced by reacting 2with the PEG-bound imidazole.

According to the literature method [59], MeO–PEG₄₀₀ and MeO-PEG₇₅₀ were tosylated, respectively, to give 3a and 3b (Scheme 1). Treating 3 with imidazole in the presence of sodium hydride produced the PEG-bound imidazoles [4a: n = 7 (average); 4b: n = 15 (average)] in 76-86 % yields. Usually, compound 2 is treated with excess of 1-substituent-imidazole derivative to prepare ferrocenyl-imidazolium salts. However, it was found to be tedious to separate the excess of 4 from the product 5 by chromatography. Instead, 2 was used in excess and the ferrocenylphosphine imidazolium salts conjugated PEG were isolated in the yields of 88 % for 5a and 67 % for 5b based on 4a and 4b, respectively. The imidazolium salts 5 are stable under nitrogen and in the air to some extent, which were actually purified in the air, and have been characterized by ¹H and ³¹P NMR spectra and API-MS.

In the ¹H NMR spectra of **5** the carbenic protons were observed in the range of δ 9.0–9.3 due to the highly acidic character of 2-proton of imidazolium ions. The length of PEG was estimated by the comparison of the area of δ 3.55–3.80 contributed from the CH₂ groups of the PEG-linkage with that at δ 6.0 from CH linked to ferrocene, consisting with the starting material MeO–PEG₄₀₀ and MeO–PEG₇₅₀ used for preparing **5a** and **5b**, respectively. The consistence could also be visualized in the API–MS of **5**, showing a series of peaks with the mass difference of 44 for each OCH₂CH₂-fragment and the richest *m/z* ion peak at 787 for **5a** relating to *n* = 7. A singlet ³¹P{¹H} NMR peak observed around δ –26.6 for **5** is expected for ferrocenyldiphenylphosphine and the value is close to that of the known compound **1** [55, 56].

2.2 Generation of the Palladium Catalyst In Situ

Some of palladium(II) complexes ligated with ferrocenylphosphine–imidazolium salt **1** have been isolated and characterized [55, 56], and it was found that the activity of the isolated palladium complexes is comparable to those of the catalyst generated in situ for Suzuki–Miyaura and Buchwald–Hartwig reactions [57]. Before taking the



Scheme 1 Synthesis of NHC precursors tethered with PEG

Entry	ArX	Product	Ligand	Pd (mol%)	Time	Yield (%) ^a
					(h)	
1	Me-Br	Me	5a	0.1	3	95
2	Me	Me	5b	0.1	3	90
3	Me	Me	1a	0.1	3	93
4	MeO-Br	MeO-	5a	0.1	3	95
5	MeO-Br	MeO-	5b	0.1	3	85
6	MeO-Br	MeO-	1a	0.1	3	95
7	F ₃ C-Cl	F3C	5a	2	21	47 ^b
8	F ₃ C-Cl	F3C	1a	2	21	52 ^c

Table 1	Influence	of PEG-linkage	on palladium	n-catalyzed	Suzuki-Miyaura	reactions of ary	l halides wit	h phenylboronic	acid in 1,4-	dioxane
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Reaction conditions: Aryl halide (5.0 mmol), phenylboronic acid (914 mg, 7.5 mmol), K_2CO_3 (1,382 mg, 10 mmol), 1,4-dioxane (10 mL), Pd(OAc)₂:ligand = 1:1.1, 110 °C (oil bath)

^a Isolated yield

^b GC yield calculated using decane as an internal standard

^c Using NaOBu^t as base

advantage of generating catalyst in situ, however, it was still a concern of coordination ability of **5** to palladium center due to the PEG chain presented. Treating Pd(OAc)₂ with an equivalent of **5a** and excess of K₂CO₃ in 1,4-dioxane at 60 °C for 0.5 h, the peak at δ 9.28 for 2-proton of imidazolium disappeared in ¹H NMR spectrum and the peak of ³¹P resonance shifted from δ –26.6 for **5a** down to δ –1.0 in the ³¹P NMR spectrum. These facts suggested that a palladium complex coordinated by NHC and phosphine was formed.

2.3 Influence of PEG Chain on the Palladium-Catalyzed Suzuki–Miyaura Reaction in Organic Solvent

Before studying on the PEG-bound salts **5** in palladiumcatalyzed Suzuki–Miyaura reaction in water, the catalytic activity of **5** in 1,4-dioxane was compared firstly with **1a** for evaluating the influence of the PEG chain. For comparison, the catalysts from both **1a** and **5** were generated by treating Pd(OAc)₂ with an equivalent of ligand and excess of K_2CO_3 in 1,4-dioxane at 60 °C for 0.5 h, by this way the coordination of NHC to palladium has been suggested as stated in the above section and also by comparing the catalytic activities with those previously reported [56].

As can be seen from Table 1, the PEG-bound ferrocenylphosphine-imidazolium salts **5** as ligand gave the catalyst with activity comparable to that of **1a** (entries 3, 6, and 8); for 4-methyl- and 4-methoxy-phenylbromide coupling with phenylboronic acid using K_2CO_3 as base, nearly quantitative conversions were achieved at 0.1 mol% of Pd loading at 110 °C after 3 h, and the desired biaryls were isolated in excellent yields (entries 1,2, and 4,5). For aryl chloride substrate with electron-withdrawing group, 47 % of conversion was achieved using **5a** as ligand at 2 mol% loading of catalyst (entry 7), comparable to 52 % using **1a** (entry 8) within experimental errors. These results mean that the PEG chain up to 15 of OCH₂CH₂ groups has not been found negative effects on their palladium catalysts.

2.4 Suzuki–Miyaura Reaction Carried Out in Aqueous Solvents

After the palladium catalyst was formed in situ, 1,4-dioxane was removed under reduced pressure and replaced with aqueous solvents to evaluate the catalytic performance. In the coupling of 4-bromotoluene with phenylboronic acid in the presence of 1 mol% catalyst in water, it was found that 42 % of conversion of 4-bromotoluene was shown for 5a (Table 2, entry 1) and 67 % for **5b** (entry 2), respectively. The lower activity compared to those in 1,4-dioxane could be ascribed to the low solubility of 4-bromotoluene in pure water, which is consistent with the findings by Shaughnessy et al. [40] using water-soluble alkylphosphines as ligands for Suzuki-Miyaura coupling of aryl bromides. To our delight, as PEG₄₀₀ was added as co-solvent in 1:1 ratio in weight, the activity was recovered to the level in 1,4dioxane and nearly quantitative conversion was achieved for 5a (entry 5) and 5b (entry 6) at 0.1 mol% of catalyst loading although longer reaction time was needed for 5a as ligand.

It is attractive to investigate PEGs as a reusable solvent medium for organic reactions [60], including for crosscoupling reactions [61, 62], because of its ready availability, low volatility, and potential for recycling catalyst. Recently, it was found that ligand-free Heck reaction of aryl bromides can be catalyzed with Pd(OAc)₂ in PEG₂₀₀₀ at the catalyst loading of 1 mol% [63]. However, without **5** as supporting ligand only 61 % of conversion was achieved for 4-bromotoluene at 1 mol% of Pd(OAc)₂ loading in PEG₄₀₀/water (1:1) (entry 4). This demonstrated that the NHC as supporting ligand is essential for the catalytic efficiency performed in the aqueous solvents.

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2.5 Effect of Base for the PEG-Bound Catalyst System

Base plays a crucial role in the palladium-catalyzed Suzuki–Miyaura reaction and it is necessary to match bases with different catalysts. A brief investigation of base influence for the PEG-bound **5b**/Pd(OAc)₂ system in aqueous solvents was carried out and the results are summarized in Table 3. In the coupling of 4-bromotoluene with phenylboronic acid in aqueous solvents, the system matches well with many bases, among which the best ones are Cs₂CO₃ and K₂CO₃ (entries 1 and 2). KF, which is frequently used in palladium-catalyzed Suzuki–Miyaura coupling reaction, showed moderate activity with 70 % conversion (entry 8). It should be noted that K₃PO₄ and KOAc are also excellent bases for the PEG-bound **5b**/Pd(OAc)₂ system with 89–97 % of conversions within 1 h (entries 6 and 7).

 Table 2
 Pd(OAc)₂/5
 catalyzed
 Suzuki–Miyaura
 coupling
 of
 4-bromotoluene with phenylboronic acid in aqueous solvents

Entry	Co-solvent (%)	Ligand	Pd (mol%)	Time (h)	Conv (%) ^a
1	_	5a	1	6	42
2	_	5b	1	6	67
3	PEG ₄₀₀ (50)	5b	1	1	>99
4	PEG ₄₀₀ (50)	_	1	6	61
5	PEG ₄₀₀ (50)	5a	0.1	6	>99
6	PEG ₄₀₀ (50)	5b	0.1	3	>99

Reaction conditions:4-Bromotoluene (855 mg, 5.0 mmol), phenylboronic acid (914 mg, 7.5 mmol), K_2CO_3 (1,382 mg, 10 mmol), water (15 mL), Pd(OAc)₂:ligand = 1:1.1, 110 °C (oil bath)

^a GC conversion was calculated using decane as an internal standard

Table 3 Effect of the base on Pd(OAc)₂/5b catalyzed Suzuki reaction of 4-bromotoluene with phenylboronic acid in aqueous solvents

Entry	Base	Time (h)	Conv (%) ^a
1	Cs ₂ CO ₃	1	>99
2	K ₂ CO ₃	1	>99
3	Na ₂ CO ₃	1	91
4	КОН	1	98
5	NaOH	1	66
6	K ₃ PO ₄	1	97
7	KOAc	1	89
8	KF	1	70

Reaction conditions: 4-Bromotoluene (172 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), base (2.0 mmol), water (2.5 mL), PEG_{400} (2.5 g), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **5b** (15.6 mg, 0.011 mmol), 110 °C (oil bath)

^a GC conversion calibrated with decane as an internal standard

2.6 Scope of the System **5b**/Pd(OAc)₂ in Aqueous Solvents

As shown in Table 4, the procedure employing $5b/Pd(OAc)_2$ as catalyst is effective in coupling a range of aryl bromides with phenylboronic acid in the presence of 0.1 mol% catalyst

using K_2CO_3 as base in aqueous solvents. For the deactivated substrate 4-bromoanisole 94 % of the isolated yield for the desired product was realized within 3 h at 110 °C (entry 8). Excellent yields in the range of 92–95 % were achieved for phenyl, 3-methylphenyl, and 4-methylphenyl bromides (entries 2, 4-6). For the substrate with *ortho*-substituent

Table 4 5/Pd(OAc)₂ catalyzed Suzuki-Miyaura reaction of aryl bromides with phenylboronic acid in aqueous solvents

Entry	Aryl bromide	Product	Ligand	Time (h)	Yield $(\%)^a$
1	Me Br	Me	5b	3	95
2	Me	Me	5a	6	95
3	F ₃ C Br	F ₃ C	5b	3	90
4	Br		5b	3	92
5	Me	Me	5b	3	92
6	Me	Me	5b	3	95
7	Me	Me	5b	3	93
8	MeO-Br	MeO	5b	3	94

Reaction conditions: Aryl bromide (5.0 mmol), phenylboronic acid (914 mg, 7.5 mmol), K_2CO_3 (1.38 g, 10 mmol), water (10 mL), PEG-400 (10 g), Pd(OAc)₂ (1.1 mg, 0.0050 mmol), **5** (0.0055 mmol), 110 °C (oil bath)

^a Isolated yield

(entry 7) excellent yield was observed as well. As expected, the catalyst system is highly effective for aryl bromides with electron-withdrawing substituents (entries 1 and 3).

3 Conclusion

In summary, the ferrocenylphospine–imidazolium salts conjugated with different length of PEG chains have been synthesized, and their structures along with those of their palladium catalysts have been characterized by ¹H and ³¹P NMR spectra and API–MS measurement. The palladium catalysts supported by the PEG-bound phosphine–carbene ligand are efficient for Suzuki–Miyaura coupling reaction of aryl bromides with phenylboronic acid in both organic and aqueous solvents, although PEG₄₀₀ as co-solvent is crucial for the catalyst activity in aqueous solvents through increasing the solubility of aryl bromides used.

4 Experimental

4.1 General Considerations

All aryl bromides and chlorides (Aldrich or Acros) were used as received. Palladium acetate was purchased from Strem Chemical Company. 1,4-Dioxane and THF were distilled under nitrogen from sodium benzophenone ketyl prior to use. Cs₂CO₃, K₂CO₃, Na₂CO₃, KF, NaOBu^t, K₃PO₄ and NaOH were used as received. All reactions and manipulations involving air- and/or moisture-sensitive compounds were carried out using standard Schlenk technique under nitrogen. NMR spectra were recorded on a BRUKER DRX 400 MHz or Varian INOVA 400 MHz (400 MHz for ¹H NMR; 162 MHz for ³¹P NMR) spectrometers. Mass spectroscopies (HRMS, API) were obtained on a Micromass Q-Tof Micro (Micromass Inc., Manchester, England).

4.2 Preparation of Ligand

4.2.1 Synthesis of MeO-PEG₄₀₀-Imidazole (4a)

A mixture of sodium hydride (0.45 g, 13 mmol) and imidazole (0.60 g, 8.8 mmol) in 20 mL of freshly distilled THF was stirred for 30 min at rt. To the mixture a solution of PEG₄₀₀-tosylate **3a** (5.80 g, 11 mmol), which was synthesized according to a procedure analogous to that previously reported [64], was added and stirred at 60 °C for 6 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (acetone–methanol from 5:1 to 2:1, V/V). Yield 76 %, yellow liquid. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 3.38 (s, 3 H), 3.56–3.76 (m, 28 H), 4.12 (t, J = 5.2 Hz, 2 H), 7.01 (br, 1 H), 7.04 (br, 1 H), 7.55 (br, 1 H).

4.2.2 *MeO*–*PEG*₇₅₀–*imidazole* (4b)

4b was prepared according to that for **4a**. Yield 86 %, yellow liquid. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 3.38 (s, 3 H), 3.55–3.76 (m, 64 H), 4.12 (t, J = 5.2 Hz, 2 H), 7.01 (br, 1 H), 7.04 (br, 1 H), 7.58 (br, 1 H).

4.2.3 Synthesis of MeO-PEG₄₀₀-Imidazolium Salt (5a)

A mixture of **2** (1.5 g, 3.3 mmol) and **4a** (1.1 g, 2.7 mmol) in CH₃CN (20 mL) and water (5 mL) was stirred at 50 °C for 48 h. Volatiles were evaporated and NaI (3.0 g, 20 mmol) was added along with 20 mL of EtOH. The mixture was stirred at 35 °C for 12 h. The solvents were evaporated and the residue was redissolved in CH₂Cl₂ and filtered through Celite. Flash column chromatography [dichoromethane-methanol (10/1, V/V)] afforded **5a** in 88 % yield as an orange liquid. ¹H NMR (CDCl₃,400 MHz,TMS): δ 2.07 (d, J = 7.4 Hz, 3H), 3.47 (s, 3 H), 3.57–3.73 (m, 28 H), 3.92–4.97 (m, 8 H), 5.95–6.00 (m, 1 H), 6.85–7.45 (m, 12 H), 9.28 (m, 1 H); ³¹P {¹H} NMR (CDCl₃, 161 MHz): δ –26.6.

4.2.4 MeO-PEG₇₅₀-Imidazolium Salt (5b)

5b was prepared according to that for **5a** in 67 % yield as an orange liquid. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.05 (d, J = 6.8 Hz, 3 H), 3.38 (s, 3 H), 3.57–3.65 (m, 64 H), 4.00 (t, 2 H, J = 6.4 Hz), 3.92–4.94 (m, 8 H), 5.95–6.05 (m, 1 H), 6.64–7.45 (m, 12 H), 9.05 (s, 1 H); ³¹P {¹H} NMR (CDCl₃, 161 MHz): δ –26.7.

4.3 Suzuki-Miyaura Coupling Reaction

4.3.1 General Procedure

In air, imidazolium salt, $Pd(OAc)_2$ and base (2 equiv of based on aryl halide) were added to an oven-dried Schlenk tube equipped with a stir bar. The Schlenk tube was fitted with a rubber septum, evacuated, and then refilled with nitrogen. 1,4-Dioxane (5.0 mL) was added via syringe. The mixture was stirred for 30 min at 60 °C for generating NHC-coordinated palladium complex. If the catalytic reaction was carried out in aqueous solvents, 1,4-dioxane was evaporated under reduced pressure. Then aryl halide, phenylboronic acid (1.5 equiv), and decane were added. The tube was sealed and immersed in a silicon oil bath at 110 °C and the course of the reaction was complete, the product was extracted with ether for three times, purified by column chromatography, and identified by ¹H NMR.

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