Synthesis of a carbene transfer organometallic polymer and application to forming a recyclable heterogeneous catalyst for the Suzuki reactions of aryl chlorides†

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An efficient and versatile synthetic approach to NHC-based organometallic polymers has been developed by a simple three-step synthesis. A novel brush polymer having imidazolium salt side chains (**P2**) was firstly synthesized through postpolymerization modification of **P1**, which permits access to Ag(I)–NHC-based side chain polymer (**P3**) at room temperature in high yield. **P3** was applied as a carbene transfer agent to form a Pd–NHC-containing polymer (**P4**) by the transmetallation reaction of Ag(I)–NHCs in the side chains. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis indicated that 77% of Ag(I)–NHCs in the side chains of **P3** were transmetallated. The resulting Pd–NHC-containing polymer (**P4**) showed high catalytic activity and reusability in the Suzuki reactions of aryl chlorides and aryl boronic acids. This novel Pd–NHC-containing polymeric catalyst was used five times and still remained active giving the desired biaryl products in 70% yield in the fifth run of the cross-coupling reaction of deactivated 4-chloroanisole with phenylboronic acid.

1. Introduction

The incorporation of transition metals into polymers have received a great amount of attention due to the unusual and attractive physical and chemical properties that these organometallic materials possess.[1] Recent investigations show that transition metal-containing macromolecules may be useful as catalysts,[2] sensors,[3] electroactive films,[4] non-linear optical devices[5] and liquid crystals.[6] The production of these kinds of polymers has been encouraged by supplying new materials with desirable properties. Significant advances have been achieved in recent years in methodologies for the preparation of transition metal-containing polymers, as exemplified by the olefin and alkyne polymerization, and ring-opening and coordination polymerizations.[7] However, further developments of novel versatile synthetic strategies giving high yields and employing mild reaction conditions are still highly desirable.

Since the discovery of stable carbenes by the groups of Bertrand[8] and Arduengo,[9] N-heterocyclic carbenes (NHCs) have attracted considerable interest in coordination chemistry and catalysis.[10] However, comparatively little attention has been directed towards developing effective synthetic approaches to functional organometallic macromolecular materials that contain NHC moieties.[11] Considering their structural diversity and capability to form stable complexes with a large number of transition metals,[12] NHCs are interesting components to construct organometallic polymeric materials. Pioneering work introducing metal–NHCs into polymers was performed by Bertrand and co-workers, who described a polymeric silver–biscarbene compound based on trialkylated 1,2,4-triazoles.[13] Recently, Bielawski's group carried out a program on using NHCs as key components to synthesize novel organometallic macromolecules,[11,14] which were based on linearly opposed bis(imidazolium) salts by incorporating transition metals into the main chains. Among those reported, the metal–NHC moieties were all located in the backbone of the polymers. Although macromolecules with organometallic moieties in the side chains are an important class of transition metal-based polymers,[15–17] metal–NHC-based side chain polymers are scarce. Hitherto only a few examples of polymer-supported catalysts that have metal–NHC moieties in parts of the side chains have been reported.[16]

Ag(I)–NHC complexes, which are readily generated by treatment of the imidazolium salt with silver oxide under mild conditions, have proved to be effective carbene transfer agents[18] for the preparation of various NHC complexes of other metals, such as palladium(II),[19] rhodium(I),[20] rhodium(III),[21] iridium(III),[21] copper(I),[22] copper(II),[23] ruthenium(II),[24] ruthenium(III),[25] ruthenium(IV),[26] nickel(II),[27] and platinum(II).[28] Notably, carbene transfer reactions proceed rapidly at ambient temperature, afford excellent yields, and are especially suitable for preparing carbene complexes, which are hard to synthesize by conventional methods.[19] However, to the best of our knowledge, only one example has been reported on the application of the transmetallation of Ag–NHC units for the construction of a tailored organometallic–inorganic hybrid mesostructured material.[29] We envisioned that if a soluble Ag(I)–NHC-based side chain polymer could be synthesized, then it might be further utilized as a carbene transfer agent to prepare a functional NHC-based organometallic polymer with higher metal loading. This would be a general and versatile synthetic approach to

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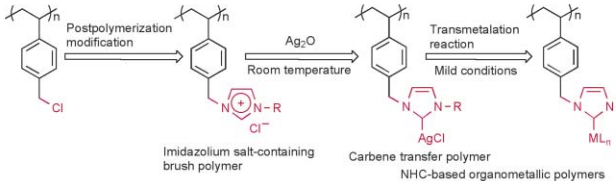
† Electronic supplementary information (ESI) available: IR spectra of **P1**, **P2**, **P3**, **P4** and recovered **P4**; Pd_{3d}, Ag_{3d}, C 1s, N 1s, O 1s and Cl 2p XPS spectra of **P4**; analytical data for products of the Suzuki cross-coupling reactions of aryl chlorides and aryl boronic acids. See DOI: 10.1039/b904944b

NHC-based organometallic polymers (Scheme 1). Herein we describe the synthesis of a novel soluble Ag(I)–NHC-based side chain polymer by postpolymerization modification of polychloromethylstyrene, and its application in the synthesis of the Pd–NHC-containing polymer by the transmetallation reaction of the Ag(I)–NHC moieties. The resulting Pd–NHC-containing polymer showed high catalytic activity and reusability in the Suzuki reactions of the challenging, relatively inactive aryl chlorides and aryl boronic acids.



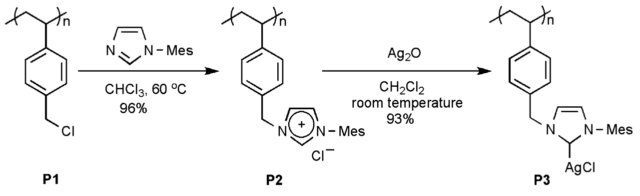
Scheme 1 General depiction of a versatile synthetic approach for preparing novel imidazolium salts containing brush polymer and NHC-based organometallic polymers.

2. Results and discussion

2.1. Postpolymerization modification for preparation of brush polymer (P2) and the Ag(I)–NHC based side chain polymer (P3)

One of the most appealing synthetic approaches to polymers containing side chains connected to a linear backbone (brush polymer)[30] is postpolymerization modification, in which the synthetic difficulties are greatly reduced by using common polyolefins as starting materials, and then altering the existing functional side chain groups to achieve the desired function.[31] The inexpensive, readily available, chemically inert polychloromethylstyrene (**P1**), can be easily modified through the benzyl chloride group by nucleophilic substitution with various nucleophilic reagents, and is therefore an ideal functional linear polymer for postpolymerization modification.[32]

For the preparation of the brush polymer having imidazolium salt side chains (**P2**), the "grafting onto" method,[33] one of the postpolymerization modification strategies, was applied to modify the side chains of **P1** (Scheme 2). Following a literature procedure,[34] **P1** ($M_n = 2.8 \times 10^4$ Da, PDI = 2.1; relative to polystyrene standards) was prepared by radical polymerization of *p*-chloromethylstyrene. Reaction of **P1** with excess 1-(mesityl)imidazole in chloroform at 60 °C for two days gave **P2**. The pendent benzyl chloride moieties along the backbone of **P1** appeared to be completely consumed as confirmed by the ^{1}H NMR spectrum of **P2**, where the characteristic peak of the 2H-imidazolium proton at 10.59 ppm (Fig. 1) appeared, and the signal typically found at δ 4.51 ppm (attributable to the CH$_2$ unit of the benzyl chloride of **P1** in CDCl$_3$) was shifted downfield to 5.3 ppm (CH$_2$ unit of the benzyl imidazolium). This is corroborated by the absence of the characteristic frequency of the CH$_2$–Cl wag of **P1** at 1264 cm^{-1} in the IR spectrum of **P2** (see ESI†).[35] The appearance of new bands at 1545 and 1449 cm^{-1} frequencies can be assigned to ν(C=N) of imidazolium.[36]



Scheme 2 Synthetic route to the imidazolium salts containing brush polymer (**P2**) and the Ag(I)–NHC based side chain polymer (**P3**).

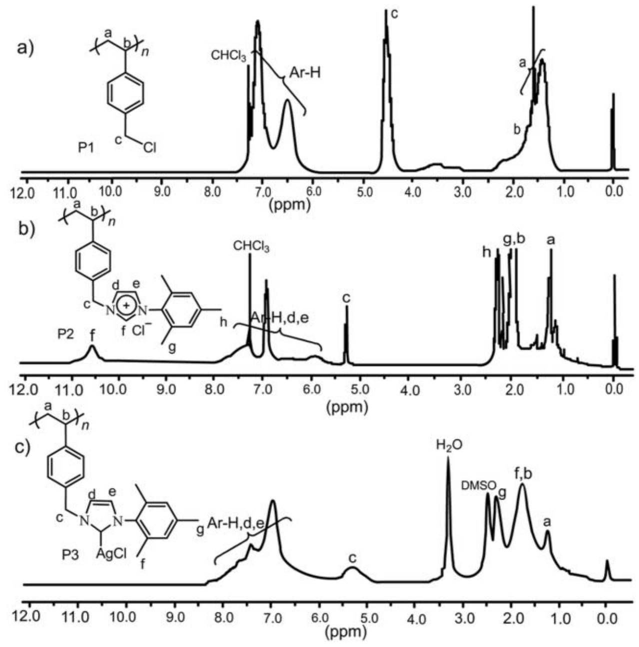


Fig. 1 ^{1}H NMR spectra of **P1**, **P2** measured in CDCl$_3$ and **P3** measured in DMSO-d_6.

Ag(I)–NHC-based side chain polymer **P3** was readily prepared by the reaction of **P2** with 1/2 equivalent of Ag$_2$O in dichloromethane using Wang and Lin's procedure.[37] After stirring for three days at room temperature, the black silver(I) oxide completely disappeared, and workup of the solution gave **P3** in 93% yield as a white air-stable solid. The formation of **P3** was established by spectroscopic techniques. The signal (10.59 ppm) corresponding to the 2H-imidazolium proton was absent in the ^{1}H NMR spectrum of **P3** (Fig. 1), which demonstrates that silver was attached quantitatively and specifically at the C2 position of the imidazolium moieties on **P2**. This was further supported by the ^{13}C NMR spectra of **P3** (Fig. 2), where a broad single resonance around 180 ppm was assigned diagnostically to C2 of the imidazol-2-ylidene carbon.[38] To our great delight, **P3** was soluble in solvents such as CH$_2$Cl$_2$, CHCl$_3$, methanol, DMF and DMSO. It should be noted that we can not rule out the possibility of cross-linked structures in **P3** such as (NHC)$_2$Ag–Cl and (NHC)$_2$Ag–Ag–Cl$_2$, although it is less possible due to its solubility in many organic solvents. As a result of its good solubility, a general approach for preparing other NHC-based side chain organometallic polymers can be developed by the transmetallation reaction of Ag(I)–NHCs in the side chains of **P3**.

2.2. Transfer strategy for preparing palladium–NHC-containing polymer (P4)

We first investigated the direct metallation reaction of **P2** with Pd(OAc)$_2$ in DMSO.[39] Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the Pd content in the

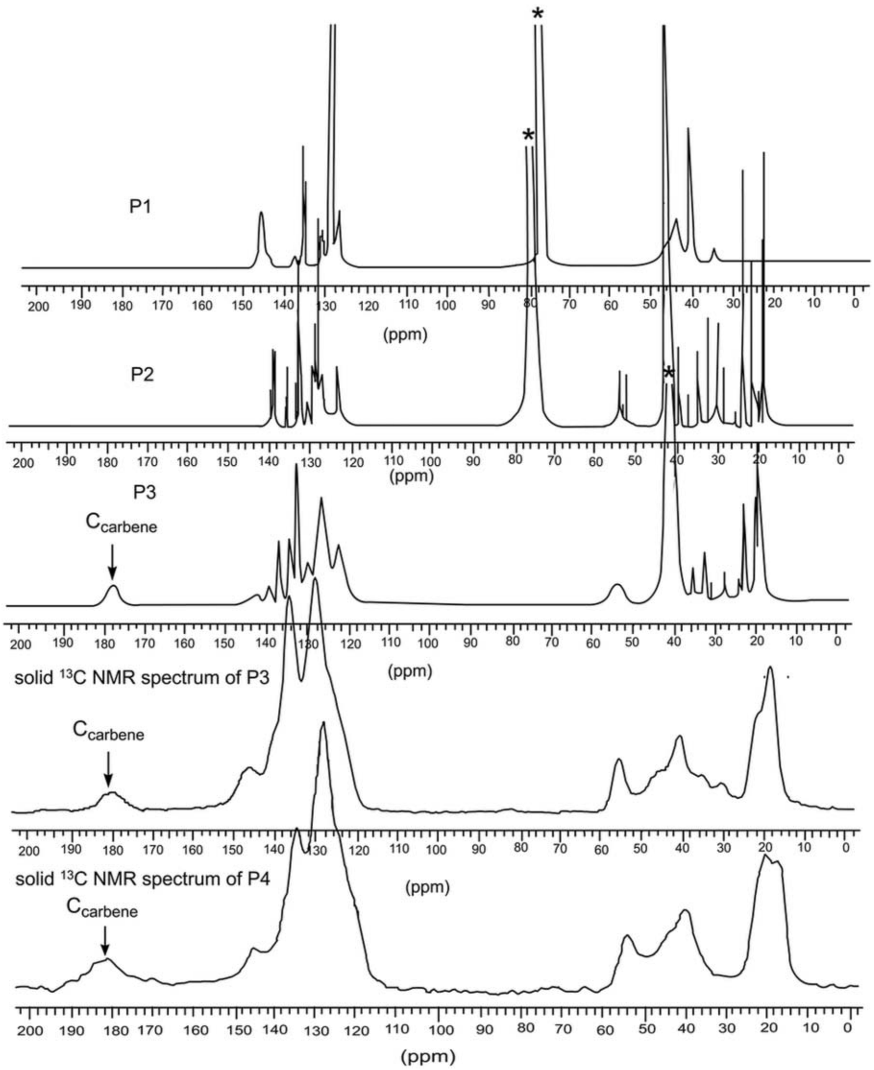
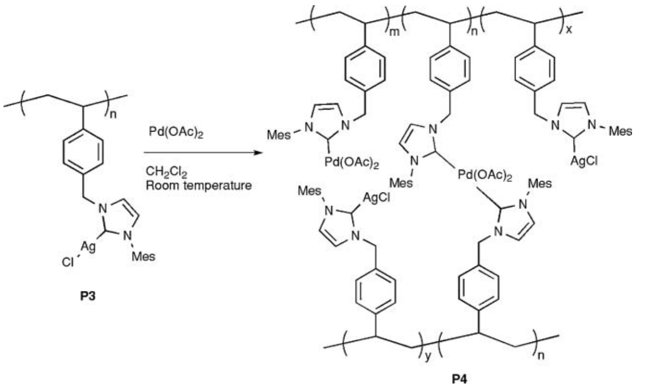


Fig. 2 ^{13}C NMR spectra of **P1**, **P2** measured in $CDCl_3$ and **P3** measured in DMSO-d_6, and the solid ^{13}C NMR spectra of **P3** and **P4**, those of the solvent are marked with asterisks (*).

resulting product was only 0.04 mmol g^{-1}. We also performed the reaction in the presence of excess NaOAc at 110 °C, 0.51 mmol g^{-1} palladium loading was found in the final polymer by ICP-AES analysis. These results showed that the direct metallation is not very effective in this case. We then turned our attention to the transmetallation strategy using Ag(I)–NHCs for synthesizing the desired Pd–NHC-containing polymer with higher palladium loading (Scheme 3). Treatment of **P3** with an excess amount of $Pd(OAc)_2$ in CH_2Cl_2 at room temperature resulted in immediate formation of white precipitate. After stirring for four days, the precipitates were filtered off. Removal of solvent from the filtrate and washing with ether afforded **P4** as an orange-brown powder. ICP-AES analysis indicated that the Ag and Pd contents were 0.52 and 1.49 mmol g^{-1} respectively in **P4**, which means that 77% of Ag(I)–NHCs in the side chains of **P3** were transmetallated. The IR spectrum (see ESI†) was used to identify the functional groups in **P4**. The two major peaks centred at 1577 and 1414 cm^{-1}, could be attributed to symmetric and unsymmetric stretching vibrations of the COO^- group,[35] demonstrating the presence of acetate in the final transmetallated product. The wide-survey



Scheme 3 Transfer strategy for preparing functional palladium–NHC-containing polymer (**P4**).

X-ray photoelectron spectroscopy (XPS) of **P4** (Fig. 3) reveals the predominant presence of carbon, oxygen, nitrogen, chlorine, palladium and silver. The observed Pd $3d_{5/2}$ and Pd $3d_{3/2}$ at 337.61 and 343.03 eV are characteristic of Pd^{2+} species (see ESI†).[40]

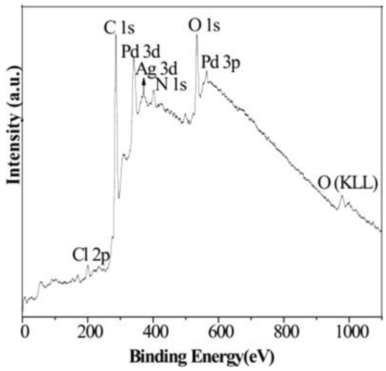


Fig. 3 The wide-survey XPS spectrum of **P4**.

The binding energy of Ag_{3d} is located at 368.28 eV.[41] The 2p photoelectron peak appearing at 198.52 eV is characteristic of Cl^{-1} (see ESI†).[42] Based on these features, the coordination modes of Pd to NHC and carboxylate,[43] and the low solubility, a cross-linked structure might be proposed for **P4** (Scheme 3). The solid state ^{13}C NMR spectrum of **P4** gives valuable information for confirming the structure, in which the boader signal around 181 ppm demonstrates the multiple carbene–metal environments in **P4** (Fig. 2).

The size and morphology of **P4** were examined by scanning electron microscopy (SEM). Fig. 4(d) displays SEM images of the sandwich. Fig. 4(a) shows micron solid tubes of a sample of **P2** obtained through slowly volatilizing the solvent CH_2Cl_2 and dragging the rest of the material. Furthermore, membrane structures having a velvet surface are observed (Fig. 4(b)). Such properties make brush polymer **P2** a promising candidate for advanced materials for membranes. Thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere (Fig. 5). Thermal degradation analysis of **P2** showed that weight loss mainly started at 239 °C, and **P3** at 275 °C. Obviously, **P2** and **P3** have higher thermal stability than **P4** (173 °C). The weight residue of **P2** at 550 °C was 9.6%, whereas that of **P3** was 28%. **P4** showed a small weight loss (31%) below 550 °C.

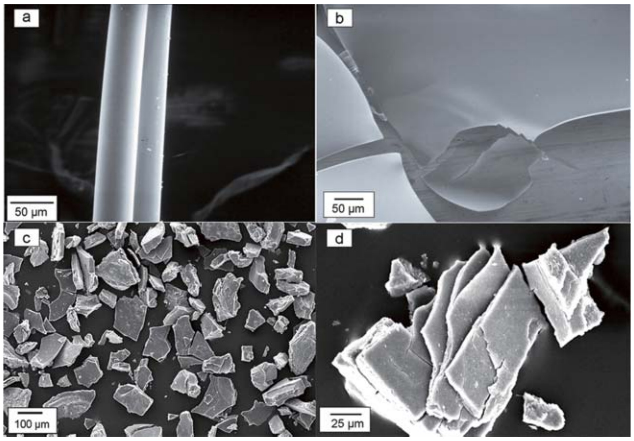


Fig. 4 SEM images of (a) micron solid tubes of **P2**, (b) membrane structures having velvet surface of **P2**, (c) the solid size of **P4**, (d) sandwich of **P4**.

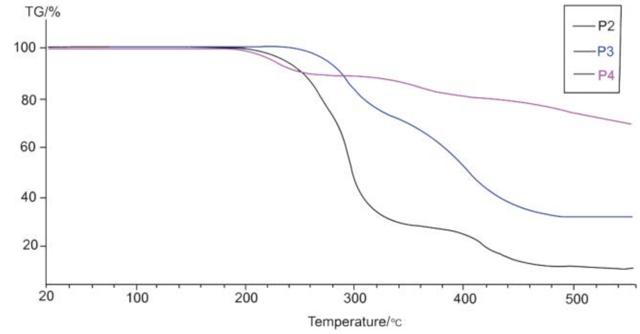


Fig. 5 Thermogravimetric curves of **P2**, **P3** and **P4** in a nitrogen atmosphere.

2.3. Catalysis of the Suzuki–Miyaura cross-coupling reactions of aryl halides with aryl boronic acids

The Suzuki reactions of aryl halides with aryl boronic acids has become an attractive standard method for the preparation of biaryl compounds in modern organic synthesis.[44] Due to the advantages of heterogeneous over homogeneous catalysis, which include the ease of product separation from the reaction mixture, the purity of the crude product and the recycling of the catalyst, numerous heterogeneous Pd catalysts have been described for the Suzuki reactions involving aryl bromides or iodides.[45] However, very limited success has been reported for the Suzuki reactions of aryl chlorides,[46] which are more challenging due to their relatively inertness. To our knowledge, examples of recyclable NHC-based heterogeneous catalytic systems for the Suzuki reactions of unreactive aryl chlorides have not been reported. Lee *et al.* recently reported a macroporous polystyrene-supported NHC–palladium catalyst for the Suzuki reactions of aryl chlorides, which only shows high reusability for the Suzuki reactions of aryl bromides.[47] In light of that, **P4** possesses much higher Pd loading and contains Ag which has been shown to enhance the catalytic activity of some Pd-catalyzed Suzuki reactions,[48] we are, thus, intrigued by the possibility of applying our Pd–NHC-containing polymer (**P4**) as a novel, active, recyclable heterogeneous catalyst for the challenging Suzuki reactions of less reactive aryl chlorides.

An electronically rich, deactivated arylchloride, 4-chloroanisole, and phenylboronic acid were employed as substrates in the screening of the Suzuki reaction parameters (Table 1). In anhydrous THF or DMF, the conversion of 4-chloroanisole was <5% (Table 1, entries 1 and 2). Gratifyingly, **P4** (at 3.0 mol% loading of Pd) exhibited high catalytic activity with 2-propanol (IPA) as the reaction solvent. For example, switching the solvent to IPA increased the product yield to 38% using K_2CO_3 as a base (Table 1, entry 3). The yield of cross-coupling product was further increased to 72% when NaO^{t}Bu was used as a base. It should be noted that the concentration of the reaction mixture was an important factor in affecting the yield. When the catalyst concentration increased from 0.01 mol L^{-1} to 0.015 mol L^{-1}, the yield of the desired coupling product increased from 72% to 93% (Table 1, entry 8). The catalyst prepared by direct metallation of **P2** with $Pd(OAc)_2$ in the presence of excess of NaOAc at 110 °C gave the product under the same reaction conditions in 57% yield (Table 1, entry 9). Neither $Pd(OAc)_2$ nor AgOAc alone promoted the cross-coupling reaction in the absence of **P4** (Table 1, entries 10 and 11). However, a mixture of $Pd(OAc)_2$ and AgOAc did produce

Table 1 Reaction condition optimization on the coupling of 4-chloroanisole with phenylboronic acid[a]

Entry	Base	Time/h	Solvent	T/°C	Yield (%)[b]
1	K_2CO_3	24	DMF	100	<5
2	K_2CO_3	24	THF	70	<5
3	K_2CO_3	24	IPA	80	38
4	K_2CO_3	24	IPA–H_2O (v/v = 1/1)	80	27
5	Na_2CO_3	24	IPA	80	30
6	K_3PO_4	24	IPA	80	57
7	Cs_2CO_3	12	IPA	80	62
8	NaO^{t}Bu	12	IPA	80	72 (93)[c]
9	NaO^{t}Bu	12	IPA	80	57[cd]
10	NaO^{t}Bu	12	IPA	80	0[e]
11	NaO^{t}Bu	12	IPA	80	0[f]
12	NaO^{t}Bu	12	IPA	80	8[g]

[a] Reaction conditions: 4-chloroanisole (1.0 mmol), $PhB(OH)_2$ (2.5 mmol), **P4** (3.0 mol% Pd), base (2.5 mmol), solvent (3.0 mL). [b] Isolated yields are based on 4-chloroanisole. [c] 2.0 mL of solvent was used. [d] The catalyst (3.0 mol% Pd) was prepared by direct metallation of **P2** with $Pd(OAc)_2$ in the presence of excess NaOAc at 110 °C. The Pd loading of this catalyst is 0.51 mmol g^{-1}. [e] $Pd(OAc)_2$ (4.0 mol%) was used as catalyst. [f] **P3** (4.0 mol% Ag) was used as catalyst. [g] AgOAc (1.0 mol%) and $Pd(OAc)_2$ (3.0 mol%) were used as catalyst.

Table 2 Catalyst recycling experiments for the Suzuki reaction of 4-chloroanisole with phenylboronic acid[a]

Cycle	1	2	3	4	5
Yield (%)[b]	94	82	75	74	70

[a] Reaction conditions: 4-chloroanisole (2.0 mmol), boronic acid (5.0 mmol), **P4** (3.0 mol% Pd), NaO^{t}Bu (5.0 mmol), IPA (4.0 mL), 80 °C, 12 h. [b] Isolated yield.

the cross-coupling product, albeit the yield was low (Table 1, entry 12), which may be attributed to the presence of AgOAc.[48] Thus, an optimized reaction condition using 1 equivalent of arylchloride, **P4** (3.0 mol% of palladium, 0.015 mol L^{-1}), 2.5 equivalent of aryl boronic acid and 2.5 equivalent of NaO^{t}Bu in IPA at 80 °C was concluded as a standard condition for the Suzuki coupling reactions of aryl chlorides. Utilizing technical grade IPA as a solvent is very attractive since it is cheap and environmentally friendly.

From an economic and industrial point of view, the recyclability of a heterogeneous catalyst is very important. Taking advantage of the insolubility of **P4** in IPA, a simple filtration was sufficient to recover the catalyst. The recyclability of the catalyst was then studied in the cross-coupling reaction of 4-chloroanisole with phenylboronic acid. The results of the recycling experiments are shown in Table 2. The catalyst could be reused under the same reaction conditions after separation, washing with water, ethanol and ether and drying *in vacuo*. It was notable that the polymer still remained catalytically active after being reused four times. The coupling reaction at the fourth and fifth runs gave the desired biaryl product in 74% and 70% yields.

It is important to verify that the observed catalytic conversion is caused by the Pd–NHC-containing polymer **P4** rather than the leached palladium species. Therefore the following catalytic transformation of 4-chloroanisole was carried out under the optimized conditions. After six hours, the catalyst (**P4**) was removed from the reaction mixture by hot filtration and the desired biaryl product was obtained in 51% yield. Further treatment of the hot filtrate under the same reaction conditions did not give increased conversion. Only 0.13% of the loaded Pd leached into the hot filtrate based on elemental analysis using inductively coupled plasma mass spectrometry (ICP-MS). We also analyzed the Pd-leaching in the recycling experiments by ICP-MS. There were very low levels of Pd-leaching (about 0.33% for the first run and less than 0.1% for the fifth run) from the polymeric catalyst. To rule out the possibility that the real catalyst was the leached Pd, in addition to the "hot filtration experiment", the mercury poisoning test was carried out.[16c,49] Addition of mercury (the molar ratio of Pd to Hg was 1 : 500) did not reduce the yields of the cross-coupling product. These results confirmed that **P4** was the reactive catalyst rather than a boomerang system. The XPS spectrum showed that Pd in the recovered **P4** was still in the +2 oxidation state. The IR spectrum of the recovered **P4** indicated the absence of acetates. It is not clear what the anionic ligand is in the recovered **P4**. It may be chloride, alkoxide or hydroxide.

The Pd–NHC-containing polymeric catalyst **P4** has been successfully applied to the Suzuki reactions of various aryl chlorides and a series of aryl boronic acids under the optimized conditions (Table 3). Both electron-poor (Table 3, entries 1–4, 9) and electron-rich (Table 3, entries 5–7 and 10–15) aryl chlorides coupled in high yields with aryl boronic acids in the presence of **P4** (3.0 mol% Pd). Remarkably, even *ortho*-substituted and electronically deactivated 2-chloroanisole can be coupled with aryl boronic acids in good yields (Table 3, entries 7 and 14). In addition, the less reactive aryl boronic acids containing nitryl groups undergo the Suzuki reactions smoothly with this procedure, though the yield decreased (Table 3, entries 15 and 16).

3. Experimental

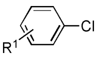
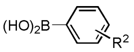
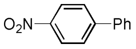
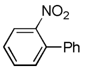
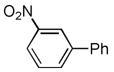
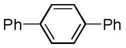
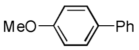
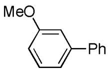
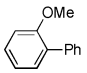
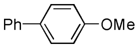
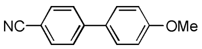
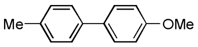
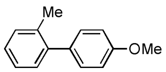
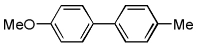
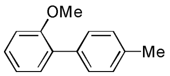
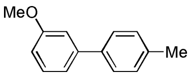
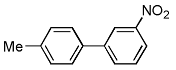
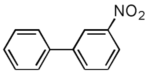
3.1. Reagents and materials

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. DMF, DMSO and IPA were used directly without further disposal. Ag_2O, $Pd(OAc)_2$, Na_2CO_3, K_2CO_3 and Cs_2CO_3 were obtained from commercial sources and directly used without further disposal. $CHCl_3$ was purified according to the method described elsewhere.[50] CH_2Cl_2 was dried over calcium hydride and freshly distilled before use. THF was dried over sodium and freshly distilled before use. 1-(Mesityl)imidazole,[51] NaO^{t}Bu was prepared by literature methods.[52]

3.2. Synthesis of P2

In a 25 mL dried Schlenk flask, **P1** (0.305 g, 2 mmol) was added to a solution of 1-(mesityl)imidazole (0.428 g, 2.3 mmol) in $CHCl_3$ (5 mL). The mixture was heated to 60 °C and stirred for 4 d. After cooling to room temperature, the solution was concentrated to 2 mL under vacuum. The white precipitate formed after the addition of 15 mL of ether, was filtered, washed several times with ether (6 × 20 mL) and dried *in vacuo* to give **P2** as a white powder (0.65 g, 96%).

Table 3 Suzuki reactions of aryl chlorides with aryl boronic acids[a]

Entry	Aryl chloride	Aryl boronic acid	Time/h	Product	Yield (%)[b]
1	 $R^1 = p$-NO_2	 $R^2 = H$	10		88
2	o-NO_2	H	10		87
3	m-NO_2	H	10		90
4	p-Cl	H	8		94[c]
5	p-OMe	H	12		93
6	m-OMe	H	12		94
7	o-OMe	H	18		91
8	H	p-OMe	10		98
9	p-CN	p-OMe	10		81
10	p-Me	p-OMe	10		84
11	o-Me	p-OMe	12		77
12	p-OMe	p-Me	12		90
13	o-OMe	p-Me	12		90
14	m-OMe	p-Me	18		84
15	p-Me	m-NO_2	12		72[d]
16	H	m-NO_2	12		75[d]

[a] Reaction conditions: aryl chloride (1.0 mmol), aryl boronic acid (2.5 mmol), **P4** (3.0 mol% Pd), NaO^{t}Bu (2.5 mmol), IPA (2.0 mL), 80 °C. [b] Isolated yields are based on arylchloride. [c] Aryl chloride (1.0 mmol), $PhB(OH)_2$ (5.0 mmol), catalyst **P4** (4.0 mol% Pd), NaO^{t}Bu (5.0 mmol), IPA (2.0 mL). [d] Homocoupling products of aryl chlorides and aryl boronic acids were detected by GC-MS.

ν(KBr)/cm^{-1}: 2924, 1609, 1545, 1487, 1449, 1373, 1197, 1158, 1067, 855, 762, 672, 553. δ_H (600 MHz; $CDCl_3$; ppm): 10.59 (br, s, N(CH)N), 6.46–7.44 (br, m, Ar-H and NCHCHN), 5.31 (br, s, NCH_2), 2.30 (br, s, p-mesityl CH_3), 2.00–2.16 (br, m, CH_2CH and o-mesityl CH_3), 1.15–1.53 (br, m, CH_2CH). δ_C (100 MHz; $CDCl_3$; ppm): 140.8–141.1 (NCHN), 127.0–139.3 (Ar-C), 123.6 (NCHCHN), 52.2–53.4 ($ArCH_2N$), 38.8–41.0 (CH_2CH), 31.5 (CH_2CH), 17.6–22.9 (mesityl CH_3).

3.3. Synthesis of P3

A mixture of **P2** (0.677 g, 2.0 mmol) and silver(I) oxide (0.232 g, 1.0 mmol) in 40 mL of CH_2Cl_2 was stirred for 3 d at room temperature. The black silver(I) oxide completely disappeared and the reaction mixture turned to a clear solution. The volume of the solution was reduced to 3 mL under reduced pressure, and 20 mL of ether was then added to produce a white solid. The solid was washed with ether (6 × 20 mL) and dried *in vacuo* to give **P3** (0.829 g, 93%).

ν(KBr)/cm^{-1}: 2920, 1609, 1556, 1489, 1448, 1411, 1236,1191, 1162, 1030, 852, 737, 681, 584. δ_H (600 MHz; DMSO-d_6; ppm): 6.99–7.47 (br, m, Ar-H and NCHCHN), 5.32 (br, s, NCH_2), 2.31–2.32 (br, s, *p*-mesityl CH_3), 1.79–2.14 (br, s, CH_2CH and *o*-mesityl CH_3), 1.13–1.68 (br, s, CH_2CH). δ_C (100 MHz; DMSO-d_6; ppm): 180.6 (C-carbene), 144.6, 138.7–140.4, 134.3–135.8, 128.3–131.2 (Ar-C), 123.0 (NCHCHN), 55.3 ($ArCH_2N$), 38.8–40.4 (CH_2CH), 31.1 (CH_2CH), 21.1 (*p*-mesity CH_3), 17.6 (*o*-mesityl CH_3). Elemental analysis: calcd: C, 56.46; H, 5.19; N, 6.27. Found: C, 56.56; H, 5.29; N, 5.74%. ICP-AES analysis: calcd: Ag, 24.15. Found: Ag, 23.43%.

3.4. Synthesis of P4

In a 100 mL dried Schlenk flask, $Pd(OAc)_2$ (0.336 g, 1.5 mmol) was added to a solution of **P3** (0.535 g, 1.2 mmol) dissolved in CH_2Cl_2 (50 mL). White precipitate immediately formed. After stirring for 4 d at room temperature, the precipitates were filtered off over Celite. An orange-brown solid was obtained after the solution was evaporated under vacuum. The product was washed with ether (6 × 20 mL) and dried in vacuum to yield 0.607 g of **P4**.

ν(KBr)/cm^{-1}: 2922, 1607, 1577, 1488, 1414, 1328, 1195, 1163, 1018, 850, 731, 690, 585 cm^{-1}. Solid ^{13}C NMR δ (75 MHz; ppm): 183.8–181.4 (br, C-carbenes), 145.5 (br), 135.2 (br), 128.7 (br), 54.1 (br), 40.2 (br), 20.3 (br, *p*-mesityl CH_3), 17.6 (br, *o*-mesityl CH_3). ICP-AES analysis: Ag, 5.61; Pd, 15.85%.

3.5. General procedure for the catalytic Suzuki reactions of aryl chlorides and aryl boronic acids

Aryl chlorides (1.0 mmol), aryl boronic acids (2.5 mmol), NaO^{t}Bu (2.5 mmol, 240 mg) and **P4** (19.8 mg, 3.0 mol% of Pd) were placed in a 15 mL dried Schlenk flask. IPA (2 mL) was added *via* syringe. The reaction mixture was stirred at 80 °C until complete consumption of aryl chlorides as monitored by TLC. After cooling to room temperature, the mixture was diluted with ether (5 mL), the catalyst was filtered, and washed with ether (3 × 5 mL). The filtrate was concentrated *in vacuo* and then purified through column chromatography. The filtered catalyst was rinsed with water (3 × 8 mL), ethanol (3 × 8 mL) and ether (4 × 8 mL), and then dried *in vacuo* for the next run.

3.6. Mercury poisoning test for the Suzuki reaction

4-Methoxychlorobenzene (123 μL, 1.0 mmol), phenylboronic acids (305.0 mg, 2.5 mmol), NaO^{t}Bu (240 mg, 2.5 mmol), mercury (222 μL, 15.0 mmol) and **P4** (20.2 mg, 3.0 mol% of Pd) were placed in a 15 mL dried Schlenk flask. IPA (2 mL) was added *via* syringe. The reaction mixture was stirred at 80 °C until complete consumption of 4-methoxychlorobenzene as monitored by TLC. After cooling to room temperature, the mixture was diluted with ether (5 mL), the catalyst was filtered, and washed with ether (3 × 5 mL). The filtrate was concentrated *in vacuo* and then purified through column chromatography.

3.7. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 600 MHz and Bruker Avance 400 MHz spectrometer at room temperature. FT-IR measurements were recorded on a 17OSX Fourier transform infrared spectrometer with KBr pellets. ICP-AES analysis was carried out by a IRIS Adv. XPS was performed on a XSAM 800 spectrometer using Al Kα as the excitation source (hm = 1486.6 eV) and operating at 12 kV and 15 mA. SEM was performed using a S-450 scanning electron microscope. TGA was conducted using a Netzsch Sta 449C thermal analyzer at a heating rate of 10 °C min^{-1} under a nitrogen flow. Pd-leaching was determined by ICP-MS on a VG PQ Exceu. Elemental analyses was performed on a Carlo Erba 1106 analyzer.

4. Conclusion

In summary, we have developed an efficient approach for organometallic polymer synthesis. A brush polymer containing imidazolium salts is prepared by a postpolymerization modification strategy, and permits access to a Ag(I)–NHC-based side chain polymer at room temperature with high yield. The Ag(I)–NHC-based side chain organometallic polymer was applied as carbene transfer agents to the synthesis of other metal–NHC-based organometallic polymers. This development offers a new methodology for constructing novel functional NHC-based organometallic polymers by a simple three-step synthesis under mild conditions. The Pd–NHC-containing macromolecule (**P4**) acts as an effective, recyclable heterogeneous metal–NHC catalyst for the Suzuki reactions of deactivated aryl chlorides and aryl boronic acids under mild conditions. This novel Pd–NHC-containing polymeric catalyst was used five times and still remained catalytically active. Further applications of Ag(I)–NHC-based side chain polymers as carbene transfer agents for preparing functional NHC-based organometallic polymers other than palladium organometallic polymer are under way in our group.

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