

Synthesis, characterization of *N*-heterocyclic carbene metallacrown palladium complex and catalytic activities in Suzuki and Heck coupling reaction

Jun-Wen Wang · Lin-Ying Gao · Fan-Hui Meng ·
Jing Jiao · Ling-Yan Ding · Li-Fang Zhang

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Abstract A series of new *N*-heterocyclic carbene Metallacrown palladium complexes with a highly flexible polyether-bridged chain $(\text{CH}_2\text{OCH}_2)_n$ ($n = 1-3$) have been synthesized by the reaction of the corresponding silver complexes and $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in acetonitrile. Complexes **7a,b–9a,b** have been structurally characterized. A single-crystal X-ray study of palladium complex 1,1'-(oxy-1,2-ethanediyl)bis[3-(1-naphthalenemethyl)imidazol-2-ylidene] palladium hexafluorophosphate **7a** adopt a *cis* configuration. They exhibited excellent catalytic activity in Suzuki–Miyoura and Heck coupling of aryl bromide in the presence of KOH.

Keywords Carbene ligands · Metallacrown ether · Palladium · Suzuki cross-coupling · Heck coupling

Introduction

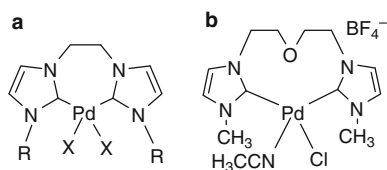
N-heterocyclic carbenes (NHCs), derived from the 1,3-disubstituted imidazolium salts, have been attracted a significant amount of research attention as a new class of ligand in a variety of metal-mediated catalytic reaction [1, 2]. NHCs have similar electron property with trialkylphosphines, but are stronger donor than the most basic phosphines. It is also easy to introduce very bulky groups on the N1 and N3 of imidazolium ring. These advantages offer a possible alternative for Pd/phosphine systems in the C–C coupling reactions. Palladium (II) complex bearing

monodentate *N*-heterocyclic carbene ligands are widely explored and used in cross-coupling reaction [3, 4]. Recently, research interest has been attracted to the synthesis of chelating ligands of *N*-heterocyclic carbene, which may provide extra air and moisture stability [5–9]. However, biscarbene are especial chelating carbene complexes have not led up to outstanding results by any reviews on the subject [10].

A variably bridging bis(imidazolium) salt for the preparation of NHC–metal complexes has been developed in which a dihalide and two molecules of *N*-substituted imidazole are used. The bridging spacer linking the two imidazolium units includes methylene, ethylene [11], *o,p*-phenylenebis(methylene) [12], pyridinediyl [13], ferrocenyl [14], oxoether and a pyridine-2,6-diylbis(methylene) linker [15]. To the best of our knowledge, only a very few reports have been made on using palladacycles of bidentate carbene complexes as catalysts in Suzuki and Heck coupling reaction. Notably, Herrmann and Fehlhhammer [16] have investigated a type of methylene-bridged chelated carbene complex. Later, Lee et al. [17] reported on the synthesis of a series of new seven-member palladacycles of bidentate carben complexes **A**, and the use of these palladium complexes with ethylene-bridged carbene in Suzuki and Heck coupling reactions. Recently, Nielsen et al. [18] investigated an ether-functionalized biscarbene complex **B**, and the palladium complexes exhibited satisfactorily as a precatalyst in a model Heck coupling reaction in presence of ${}^n\text{Bu}_4\text{NBr}$ (Scheme 1).

Recently, we reported the synthesis of a series of new silver (I) and gold (I) *N*-heterocyclic carbene metallacrown complexes (**4a,b–6a,b**) [15]. Since these complexes contain both a metal atom and a polyether chain, they can act as both a catalyst and a phase-transfer reagent. Although Polyether-chain metallacrown ethers containing phosphane

J.-W. Wang (✉) · L.-Y. Gao · F.-H. Meng · J. Jiao ·
L.-Y. Ding · L.-F. Zhang
Department of Chemistry, Shanxi Normal University,
Linfen 041004, People's Republic of China
e-mail: wjwchlwx@yahoo.com.cn



Scheme 1 Structures of the complexes **A** and **B**

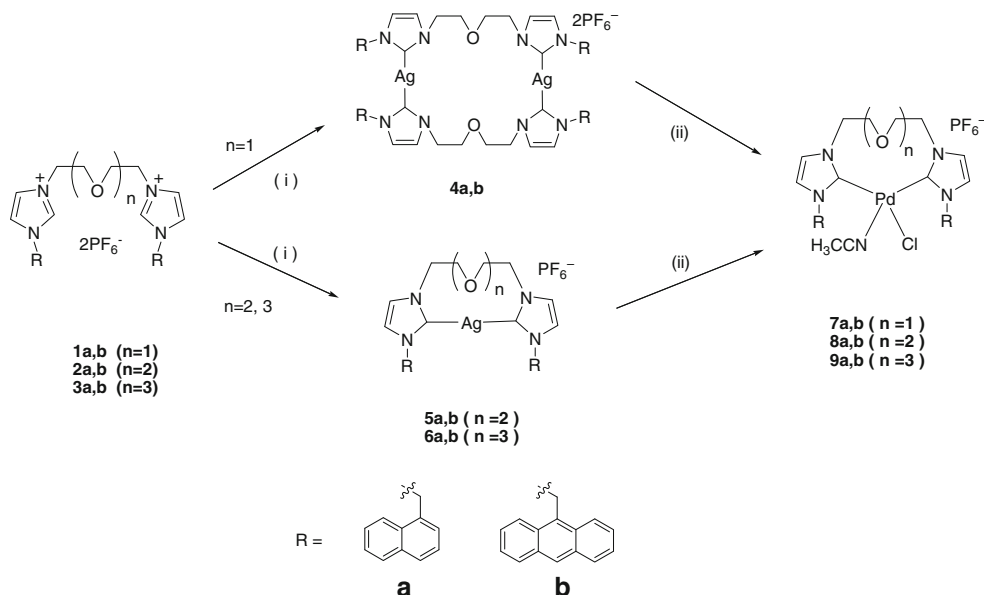
have been broadly studied [19], there was no reported on *N*-heterocyclic carbene palladium complex containing metallacrown ether. It has been established in the literature that a variety of silver–NHC complexes have been successfully transferred to other palladium-included metals by transmetalation [20]. This prompted our study on the synthesis of bidentate *N*-heterocyclic carbene palladium complexes with polyether chain and investigated whether these bidentate ligands palladium complexes are more effective catalysts in the C–C coupling reactions. Here, we describe our efforts in the preparation of the much longer oxoether-supported macrocyclic palladium complexes and their initial catalytic study in Suzuki–Miyaura and Heck coupling reaction.

Results and discussion

Ligand precursors [RHimy-(CH₂OCH₂)_{*n*}-imyHR][PF₆]₂ (R = 1-naphthylmethyl, 9-anthracenylmethyl, *n* = 1–3, **1a,b–3a,b**) were prepared by according to our previous reported procedures [15]. [RHimy-(CH₂OCH₂)_{*n*}-imyHR][I]₂ were prepared simply by refluxing the

corresponding diiodide ICH₂(CH₂OCH₂)_{*n*}CH₂I with 1-substituted imidazoles in THF. These compounds (**1a,b–3a,b**) were formed by an ion-exchange reaction with NH₄PF₆ in methanol.

The palladium (II) carbene complexes with a chelating ligand can be prepared by the reaction between palladium (II) acetate and bisimidazolium salts in DMSO, which already been widely reported [21]. We attempted to synthesize these oxoether-supported macrocyclic palladium complexes by the reaction of the above, but not a satisfactory results. The similar results have been reported in several instances [18]. However, the transmetalation reaction has been proved to be a promising procedure to obtain the chelating carbene complexes in few cases [22]. Silver–NHC complexes (**4a,b–6a,b**) were prepared according to our previous reported procedures [15]. The imidazolium salts were heated with silver(I) oxide in DMSO at 90 °C for 8 h and the resulting suspension was then filtered through Celite and water was added to the filtrate, silver–NHC complexes (**4a,b–6a,b**) were obtained in good yield (65–75%). The palladium NHC complexes (**7a,b–9a,b**) were conveniently prepared by the transmetalation reaction between silver–carbenes and PdCl₂(CH₃CN)₂ in high yields at room temperature (Scheme 2). It is worthy to note that the palladium macrocyclic complexes can be obtained in concentrated solution in a high yield. These complexes are stable to air and moisture in the solid state. They are poorly soluble in diethyl ether and petroleum ether, but readily soluble in polar solvents such as acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide, dichloromethane and acetone.



Scheme 2 Synthesis of macrocyclic palladium complexes of *N*-heterocyclic carbene. Reagents and conditions: (i) DMSO, Ag₂O, 90 °C, 8 h; (ii) acetonitrile, PdCl₂(CH₃CN)₂, room temperature, 12 h

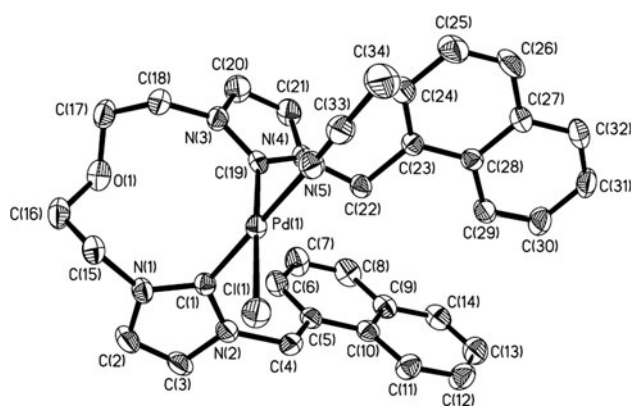


Fig. 1 Ortep plot of **7a**

Table 1 Selected bond lengths (Å) and angles (°) for **7a**

Pd(1)–C(1)	1.981(5)	Pd(1)–C(19)	1.997(5)
Pd(1)–N(5)	2.055(5)	Pd(1)–Cl(1)	2.3288(15)
C(1)–Pd(1)–C(19)	92.34(18)	C(1)–Pd(1)–N(5)	177.18(18)
C(19)–Pd(1)–N(5)	90.26(17)	C(1)–Pd(1)–Cl(1)	86.41(13)
C(19)–Pd(1)–Cl(1)	177.34(14)	N(5)–Pd(1)–Cl(1)	91.04(13)
N(3)–C(19)–Pd(1)	129.2(3)	N(4)–C(19)–Pd(1)	125.6(4)

The macrocyclic palladium complexes were fully characterized by ^1H NMR and ^{13}C NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction. The formation of the palladium carbene complexes was confirmed by ^1H NMR and ^{13}C NMR spectroscopy. The disappearances of the signals of the imidazolium protons (N–CH–N) show the formation of expected palladium carbene complexes. In the ^1H NMR (300 MHz, d_6 -DMSO, 25 °C) spectrum of the complex **7a**, one resonance was observed at $\delta = 2.03$ (single) ppm for the CH_3CN . The ^1H NMR data (d_6 -DMSO, 25 °C) supported the displacement the CH_3CN by the d_6 -DMSO donor. The eight protons of the polyether were observed at $\delta = 4.29$, 4.21, 4.1 and 3.94 ppm. In the ^{13}C NMR spectra, the characteristic coordinated C_2 signals were observed at δ 162.5, 164.2, 165.0, 165.1, 165.1 and 165.2 ppm, respectively, which has not be found in the case of Nielsen [18].

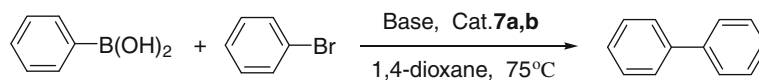
Crystals of complex **7a** suitable for X-ray crystallography were obtained by the layering of diethyl ether onto a saturated CH_3CN and chlorobenzene solution (2:1). The crystal structure of **7a** is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. The X-ray structural analysis of **7a** shows that the center palladium atom has square planer coordination geometry. As shown in Fig. 1, it consists of one molecular **7a** and one molecular acetonitrile. The bond distances of Pd(1)–C(1) and Pd(1)–C(19) are 1.981(5) and 1.997(5) Å, respectively. The bond angle of C(1)–Pd(1)–C(19) is 92.34 (18)°. The dihedral angle of two imidazolium rings is 79.1°. When compared to the

corresponding values reported for the ethylene-bridged bis(carbene) complex $[\text{Pd}(\text{carbene})\text{Br}_2]$, carbene = (1,1'-Di(1-naphthalenemethyl)-3,3'-ethylenediimidazol-2,2'-diylidene) (**10**) [13], the average Pd–C(carbene) bond length (1.986 Å) in **7a** is slight longer than that of 1.976 Å in **10**, and the angles C(carbene)–Pd–C(carbene) (92.34°) is significantly bigger than that of 84.56° in **10**. This indicate that the ten-membered palladacycles with the oxoether-bridged chain Pd(II)–NHC is quite flexible and adopt a *cis* geometry. These values were slight different with the corresponding values (1.970 and 1.999 Å) reported for the ether-functionalized biscarbene complex by Nielsen [18].

With these Pd(II)–NHC metallacrown ether complexes on hand, their catalytic abilities were evaluated. Suzuki cross-coupling reaction represents one of the most widely used C–C bond forming reactions. Although utility of the palladium/NHC systems in C–C coupling has been broadly explored [23, 24]. The chelating macrocyclic Pd(II)–NHC complex have not been extensively investigated in catalysis as monodentate NHCs, and there was no report on *N*-heterocyclic carbene palladium complex containing metallacrown ether. We started the evaluation of the catalytic activity of catalyst **7a,b** in Suzuki coupling reaction first.

Suzuki–Miyoura coupling reaction

The nature of the initial precatalyst, solvent, and base is crucial for the success of the Suzuki–Miyoura coupling reaction. The reaction condition screen demonstrated that the catalytic activity of **7a** in Suzuki cross-coupling is highly solvent and base dependent. Using toluene and phenylboronic acid as the prototypical substrate combination and, our initial base screen was carried out with catalyst **7a** and 1,4-dioxane as solvent. To our delight, the coupling product was isolated in all reaction. Among five bases examined, the use of KOH as the base in 1,4-dioxane at 75 °C gave the coupled product in 99% after 5 h (Table 2, entry 5). The other bases such as Na^tOBu , K^tOBu , Na_2CO_3 and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ gave moderate yields (Table 2, entries 1–4), so the cheap KOH was performed for the reaction. Of the solvents examined, 1,4-dioxane turned out to give the best yield. When the coupling reaction was carried out in a mixture of solvents (dioxane/ H_2O , v/v = 1:1), the yield of the coupled product was significantly decreased (Table 2, entry 6). But, using the mixtures of THF/ H_2O (1:1) and DMF/ H_2O (1:1), the yields of biaryls were increased. The similar results were found in the literature [25, 26]. In a similar fashion, by using the catalyst **7b** instead of **7a**, the similar results of Suzuki coupling reaction have been observed under same condition (Table 2, entries 1–11). Under optimized condition, all the reactions of selected the substrate were carried out at 75 °C and 5 h. The results are summarized in Table 3. As

Table 2 Screening the reaction conditions for Suzuki–Miyaura cross-coupling reaction^a

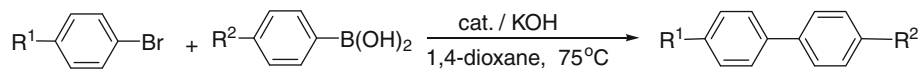
Entry	Solvent	Cat.	Base	Time (h)	Yield (%) ^{b,c}
1	1,4-Dioxane	7a,b	KO ^t Bu	5	41 (48)
2	1,4-Dioxane	7a,b	NaO ^t Bu	5	56 (60)
3	1,4-Dioxane	7a,b	Na ₂ CO ₃	5	48 (52)
4	1,4-Dioxane	7a,b	Na ₃ PO ₄ ·12H ₂ O	5	23 (25)
5	1,4-Dioxane	7a,b	NaOH	5	65 (70)
6	1,4-Dioxane	7a,b	KOH	5	99 (99)
7	1,4-Dioxane/H ₂ O (1:1)	7a,b	KOH	5	42 (50)
8	THF	7a,b	KOH	12	20 (26) ^d
9	THF/H ₂ O (1:1)	7a,b	KOH	12	30 (35) ^d
10	DMF	7a,b	KOH	5	78 (84)
11	DMF/H ₂ O (1:1)	7a,b	KOH	5	91 (93)

^a Reaction condition: 0.5 mmol of PhBr, 0.6 mmol PhB(OH)₂, 1.5 mmol of base, 1% mmol **7a,b**, 75 °C, 5 h

^b Isolated yields (**7a**)

^c Isolated yields in parentheses (**7b**)

^d Reaction conditions: 50 °C, 12 h

Table 3 Suzuki–Miyaura cross-coupling of aryl bromides with different boronic acid^a

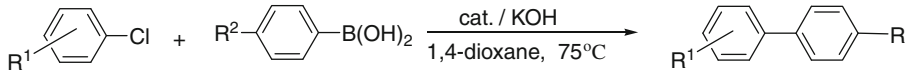
Entry	Cat.	R ¹	R ²	Time (h)	Yield (%) ^b	TON	TOF (h ⁻¹)
1	7a	H	H	5	99	99	19.8
2	7a	H	Cl	5	89	89	17.8
3	7a	H	Me	5	89	89	17.8
4	7a	H	OMe	5	99	99	19.8
5	7a	OMe	H	5	99	99	19.8
6	7a	OMe	Cl	5	99	99	19.8
7	7a	OMe	Me	5	98	98	19.6
8	7a	OMe	OMe	5	95	95	19
9	7b	H	H	5	97	97	19.4
10	7b	H	Cl	5	99	99	19.8
11	7b	H	Me	5	99	99	19.8
12	7b	H	OMe	5	86	86	17.2
13	7b	OMe	H	5	99	99	19.8
14	7b	OMe	Cl	5	99	99	19.8
15	7b	OMe	Me	5	98	98	19.6
16	7b	OMe	OMe	5	99	99	19.8

^a Reaction condition: 0.5 mmol of aryl bromides, 0.6 mmol aryl boronic acid, 1.5 mmol of KOH, 1 mol% catalyst, 75 °C, 5 h

^b Isolated yields of homogeneous samples after chromatographic purification

shown in the table 3, the combination of catalysts **7a,b**, base KOH and solvent 1,4-dioxane have been successfully employed in a series of aryl bromides and arylboronic acid at 75 °C in 5 h. All of aryl bromides and aryl boronic acid were converted to the corresponding biaryls with excellent yields, regardless of the functionality substituents (Table 3,

entries 1–16). On the other hand, we also examined the Suzuki–Miyaura coupling reaction of aryl chlorides with phenylboronic acid using these palladium macrocyclic carbene complexes. It indicates that these palladium carbene complexes are moderate active in the coupling of non-activated aryl chlorides and arylboronic acid (Table 4).

Table 4 Suzuki–Miyaura cross-coupling of aryl chlorides with different boronic acid^a


Entry	R ¹	R ²	Yield (cat. 7a) ^b	Yield (cat. 8a) ^b	Yield (cat. 9a) ^b
1	H	H	15	55	62
2	<i>o</i> -CH ₃	H	18	35	44
3	<i>p</i> -CH ₃	H	22	30	40
4	<i>p</i> -NO ₂	H	86	99	100
5	H	Me	7	27	35
6	<i>o</i> -CH ₃	Me	14	22	38
7	<i>p</i> -CH ₃	Me	22	30	39
8	<i>p</i> -NO ₂	Me	90	92	96
9	H	OMe	7	35	50
10	<i>o</i> -CH ₃	OMe	28	34	45
11	<i>p</i> -CH ₃	OMe	20	28	43
12	<i>p</i> -NO ₂	OMe	72	73	83
13	H	Cl	20	29	34
14	<i>o</i> -CH ₃	Cl	32	44	36
15	<i>p</i> -CH ₃	Cl	26	39	48
16	<i>p</i> -NO ₂	Cl	98	98	99

^a Reaction condition: 0.5 mmol of aryl chlorides, 0.6 mmol aryl boronic acid, 1.5 mmol of KOH, 1% mmol catalyst, 75 °C, 5 h

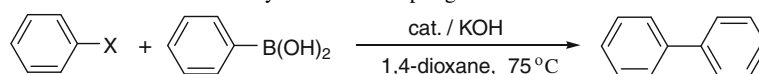
^b Isolated yields of homogeneous samples after chromatographic purification

To further probe the effect of ring size of ligand on catalytic activity, six palladium–NHC metallacrown ether catalysts, **7a,b** (10-membered palladacycles), **8a,b** (13-membered palladacycles) and **9a,b** (16-membered palladacycles), were compared in the coupling of bromobenzene and with phenylboronic acid (Table 5). As shown in Table 5, all the catalysts (**7a,b–9a,b**) gave excellent results in this simple coupling reaction of bromobenzene and phenylboronic acid. However, catalytic cross-coupling reaction of aryl chlorides with arylboronic acid provided moderate yields using these complexes **7a–9a** (Table 4, entry 1–16). We found that under identical conditions, the coupled products of the *p*-nitrochlorobenzene with arylboronic acid were obtained in higher yield and suggests the electron-poor substituent (Table 4, entry 4). The electron-rich chlorobenzene gave coupled product in moderate to low (7–55%) yields. It appears that the catalytic activities of catalysts were clear related to the size of the cycle of the palladium complexes and the nature of the substitutes (Table 4, entry 1–16). The bigger of the size of the palladacycles of the catalyst, the more activity could be observed in coupling reaction. Previous results had shown that steric bulkiness on bis(imidazolium) salts are essential for high catalytic activity, our results shows that the substituents of the imidazolidene (*N*-naphthylmethyl and *N*-anthracenylmethyl) have slight affect the catalytic activity of complexes in Suzuki coupling reaction. These may allow correlation of catalytic activity with the structure of the complexes.

Recently, Lee et al. [17] disclosed similar results, seven-member palladacycles in Suzuki and Heck coupling reactions produced comparable catalytic activities to those of six-member analogs. We have synthesized the analogous compound having the CH₂ groups in place of O atom in the chain of **7a**, and discussed the catalytic activity of the analogous compound in Suzuki cross-coupling reaction in same condition. The yields (75–90%) of the products of coupling are lower than complex **7a**. To our knowledge, only a few examples of the chelating NHC complex have been reported to perform Suzuki–Miyaura couplings under aerobic conditions [27, 28]. In 2006, Slaughter et al. [5] reported an example of Suzuki–Miyaura coupling reaction employing chelating Chugaev-type palladium NHC complexes in the presence of moisture and air at 120 °C in dimethylacetamide (DMA). To test the catalytic activity of these catalysts under aerobic conditions, we also performed the reactions under air (Table 5). Moderate yields were obtained at 75 °C in 1,4-dioxane. This suggests that the coupling reactions are better carried out in an inert atmosphere than that in air.

Heck reaction

It is noteworthy that the palladium carbene catalysts used in the initial work by Herrmann et al. [29, 30]. The Heck coupling reaction was performed in standard conditions

Table 5 Effect of NHC ligand and air on the Suzuki–Miyaura cross-coupling^a

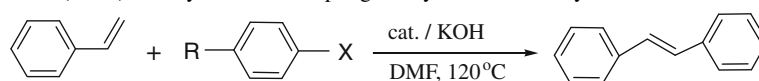
Entry	Cat.	X	Yield (%), ^{b, c}	Yield (%), ^{b, d}
1	7a	Br	99	67
2	7b	Br	97	59
3	8a	Br	99	64
4	8b	Br	94	68
5	9a	Br	99	70
6	9b	Br	99	71

^a Reaction condition: 0.5 mmol of PhBr, 0.6 mmol PhB(OH)₂, 1.5 mmol of KOH, 1% mmol catalyst, 75 °C, 5 h

^b Isolated yields of homogeneous samples after chromatographic purification

^c Reactions under N₂ conducted in 1,4-dioxane

^d Reactions under air conducted open to atmosphere in 1,4-dioxane

Table 6 NHC–Pd(II) complexes **7a,b–8a,b** catalyzed Heck coupling of aryl halide with styrene^a

Entry	R	X	Cat.	Yield (%) ^b	TON	TOF (h ⁻¹)
1	H	Br	7a	82	82	16.4
2	OCH ₃	Br	7a	84	84	16.8
3	H	Br	7b	84	84	16.8
4	OCH ₃	Br	7b	81	81	16.2
5	H	Br	8a	85	85	17
6	OCH ₃	Br	8a	85	85	17
7	H	Br	8b	88	88	17.6
8	OCH ₃	Br	8b	84	84	16.8
9	H	Br	9a	86	86	17.2
10	OCH ₃	Br	9a	86	86	17.2
11	H	Br	9b	84	84	16.8
12	OCH ₃	Br	9b	85	85	17
13	H	Cl	7a	19	19	3.8
14	<i>p</i> -CH ₃	Cl	7a	16	16	3.2
15	<i>o</i> -CH ₃	Cl	7a	13	13	2.6
16	H	Cl	7b	21	21	4.2
17	<i>p</i> -CH ₃	Cl	7b	20	20	4
18	<i>o</i> -CH ₃	Cl	7b	13	13	2.6
19	H	Cl	8a	21	21	4.2
20	H	Cl	8b	23	23	4.6
21	H	Cl	9a	22	22	4.4
22	H	Cl	9b	24	24	4.8

^a Reaction condition: 0.5 mmol of aryl halide, 0.6 mmol styrene, 1.5 mmol of KOH, 1 mol% catalyst, 120 °C, 5 h

^b Isolated yields of homogeneous samples after chromatographic purification

(polar solvent, 120–170 °C, 20 h, NaOAc). Remarkably, the biscarbene and especially chelating dicarbene complexes have been considered as catalysts for the Heck reaction. These studies also included the catalytic activity of the Heck reacting was correlated to the length, rigidity

and bulk of the substituent [31]. In the light of the above, We have started a research of the Heck coupling reaction used the *N*-heterocyclic carbene palladium metallacrown ethers (**7a,b–9a,b**) as catalysts. The Heck coupling reaction was also exploited in the presence of various bases and

solvents. We demonstrated that base KOH and solvent DMF afforded the best yield in the Heck coupling reaction of aryl bromides with styrene at 120 °C in 5 h (Table 6, entries 1–12). But, under same condition, the coupled products of aryl chloride and styrene were obtained in low yields. Nielsen et al. recently have carried out simple studies on the Heck reaction of 4-bromoacetophenone and *n*-butyl acrylate with an ether-functionalized palladium biscarbene complexes as catalyst, under standard conditions (*N,N*-dimethylacetamide (DMAc), 120 °C, 20 h, 1% mmol% catalyst) [18]. The Heck reaction product was obtained a modest yield (23%, GC yield, 20 h), with significantly increased activity obtained in the presence of ^tBu₄NBr (88%, GC yield). Independently, catalysts **7a,b–9a,b** were effective catalysts for Heck reaction of aryl bromides with styrene. The corresponding coupled products were obtained in high yields in DMF at 120 °C in 5 h (81–88%, isolated yield). It may be own to the palladium complexes had much higher stability, the increased the bulk of the substitute, and the ability of palladium metal-lacrown ether complexes acting as a phase-transfer reagent instead of ^tBu₄NBr.

Conclusions

In summary, a series of new polyether chain containing bis(carbene)Pd(II) complexes can be easily prepared by the transmetalation reaction between the corresponding Ag(I) complexes and PdCl₂(CH₃CN)₂ in acetonitrile at room temperature in excellent yields. Our preliminary results showed that these palladium complexes show excellent catalytic activity in Suzuki cross coupling reaction of aryl bromide and the activities of catalysts are clear related to the size of the palladacycles, the palladium complexes much higher stability and the increased the bulk of the substitute. In Heck reaction, these palladium catalysts are acting as a phase-transfer reagent instead of ^tBu₄NBr.

Experimental

All manipulations were performed using Schlenk techniques, and solvents were thoroughly dried and deoxygenated by standard methods. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O, hexane, 1,4-dioxane and toluene (Na), CH₂Cl₂, CH₃CN (CaH₂). **7a,b–9a,b** were prepared by according to our previous reported procedures [15]. ¹H NMR and ¹³C NMR spectra were recorded using a Varian Mercury Vx 300 spectrometer operating at 300 MHz (¹H) and 75 MHz (¹³C) in CDCl₃ and *d*₆-DMSO

with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. Elemental analyses were performed by Chemistry Department of Shanxi University.

Synthesis

1,1'-(oxy-1,2-ethanediyl)bis[3-(1-naphthalenemethyl)imidazol-2-ylidene] palladium hexafluorophosphate (**7a**)

PdCl₂(CH₃CN)₂ (38.4 mg, 0.148 mmol) was added to a solution of **4a** (110 mg, 0.074 mmol) in CH₃CN (20 mL) under argon. The solution was stirred for 12 h at the room temperature and a white precipitate was formed. After filtered through Celite the clear colorless solution was reduced to 1 mL under vacuum, and ether (15 mL) was added to precipitate a white solid. The product was collected and washed with 10 mL of ether to give 108 mg of **7a**. Yield, 90%. Anal. Calcd for C₃₄H₃₃ClF₆N₅OPPd: C, 50.14, H, 4.08, N, 8.60; Found: C, 50.10, H, 4.21, N, 8.48. ¹H NMR (300 MHz, *d*₆-DMSO, 25 °C): 7.85–8.02 (m, 6 H), 7.38–7.61 (m, 8 H), 7.05 (s, 2 H), 6.75 (d, *J* = 12.8 Hz, 2 H), 5.56 (s, 4 H), 4.29 (t, *J* = 5.6 Hz, 2 H), 4.21 (t, *J* = 5.3 Hz, 2H), 4.1 (d, *J* = 5.8 Hz, 2H), 3.94 (d, *J* = 5.6, 2 H), 2.03 (s, 3 H) ppm. ¹³C NMR (75 MHz, *d*₆-DMSO, 25 °C): δ = 162.5, 133.7, 129.3, 129.1, 128.9, 129.3, 127.4, 127.1, 126.8 (Ar-C), 124.1, 123.7, 123.4, 122.8 (im-C), 118.7 (MeCN), 72.6, 70.3 (OCH₂), 53.3 (ArCH₂N), 51.7, 50.9 (*N*-CH₂), 1.09 (*Me*CN) ppm.

1,1'-(oxy-1,2-ethanediyl)bis[3-(9-anthracenylmethyl)imidazol-2-ylidene] palladium hexafluorophosphate (**7b**)

The complex was prepared following a procedure similar to that for **7a**. A yellow powder was obtained. Yield: 91%. Anal. Calcd for C₄₂H₃₇ClF₆N₅OPPd: C, 55.15, H, 4.08, N, 7.66; Found: C, 55.10, H, 4.21, N, 7.54. ¹H NMR (300 MHz, *d*₆-DMSO, 25 °C): 8.83 (s, 1 H), 8.76 (s, 1H), 8.66 (d, *J* = 8.8 Hz, 2 H), 8.46 (d, *J* = 8.7 Hz, 1 H), 8.34 (d, *J* = 8.5 Hz, 1 H), 8.14–8.19 (m, 4H), 7.54–7.67 (m, 10H), 7.46 (d, *J* = 1.8 Hz 1H), 6.84 (d, *J* = 13.2 Hz, 2H), 6.49 (s, 2 H), 6.47 (d, *J* = 1.8 Hz, 1 H), 4.78 (t, *J* = 5.5 Hz, 2H), 4.05 (t, *J* = 5.4 Hz, 2 H), 3.82 (d, *J* = 5.2 Hz, 2 H), 3.54 (d, *J* = 5.1 Hz, 2 H) 2.08 (s, 3 H) ppm. ¹³C NMR (75 MHz, *d*₆-DMSO, 25 °C): δ = 164.2 (NCN), 135.7, 130.9, 130.7, 130.5, 130.0, 129.6, 129.6,

129.1, 127.7, 127.4, 125.4, 125.3, 124.2, 123.8 (Ar-C), 123.6, 123.2, 122.7, 122.2 (im-C), 121.3 (MeCN), 70.2, 69.5 (OCH₂), 51.0 (ArCH₂N), 46.5, 44.8 (N-CH₂), 1.02 (MeCN) ppm.

1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[3-(1-naphthalenemethyl)imidazol-2-ylidene]palladium hexafluorophosphate (**8a**)

The complex was prepared following a procedure similar to that for **7a**. A yellow powder was obtained. Yield: 94%. Anal. Calcd for C₃₆H₃₇PdClF₆N₅O₂P: C, 50.36, H, 4.34, N, 8.16; Found: C, 50.18, H, 4.50, N, 8.09. H¹ NMR (300 MHz, *d*₆-DMSO, 25 °C): δ = 8.12 (m, 4 H), 7.80 (m, 4 H), 7.16–7.54 (m, 10 H), 5.76 (s, 4 H), 4.56–4.84 (m, 4 H), 3.70–3.91 (m, 8 H), 2.02 (s, 3 H). ¹³C NMR (75 MHz, *d*₆-DMSO, 25 °C): δ = 165.02 (NCN), 133.88, 131.76, 131.21, 129.68, 129.12, 128.34, 127.41, 126.56 (Ar-C), 125.99, 124.35, 123.98, 123.57(im-C), 120.1 (MeCN), 70.96, 70.39, 69.8, 69.7 (OCH₂), 51.87(ArCH₂N), 48.3 (N-CH₂), 1.1 (MeCN) ppm.

1,1'-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[3-(9-anthracenylmethyl)imidazol-2-ylidene]palladium hexafluorophosphate (**8b**)

The complex was prepared following a procedure similar to that for **7a**. A yellow powder was obtained. Yield: 93%. Anal. Calcd for C₄₄H₄₁PdClF₆N₅O₂P: C, 55.13, H, 4.31, N, 7.31; Found: C, 55.0, H, 4.52, N, 7.48. H¹ NMR (300 MHz, *d*₆-DMSO, 25 °C): δ = 8.72 (s, 2 H), 8.61 (d, ³J_{H,H} = 8.2 Hz, 4 H), 8.12 (d, ³J_{H,H} = 8.1 Hz, 4 H), 7.64–7.52 (m, 8 H), 6.46 (d, ³J_{H,H} = 12.8 Hz, 2 H), 6.86 (d, ³J_{H,H} = 14.8 Hz, 2 H), 6.44 (s, 4 H), 4.71–4.89 (m, 4 H), 4.01 (s, 4 H), 3.71–3.81 (m, 4 H), 2.05 (s, 3 H) ppm. ¹³C NMR (75 MHz, *d*₆-DMSO, 25 °C): δ = 165.1 (NCN), 131.64, 131.44, 130.33, 129.90, 128.20, 126.16, 124.98 (Ar-C), 124.69, 124.40, 122.14(im-C), 118.1 (MeCN), 70.99, 70.32, 69.9, 69.7 (OCH₂), 51.76(ArCH₂N), 47.24 (N-CH₂), 1.3 (MeCN) ppm.

1,1'-[Oxybis(2,1-ethanediylloxy-2,1-ethanediyl)]bis[3-(1-naphthalenemethyl)imidazol-2-ylidene]palladium hexafluorophosphate (**9a**)

The complex was prepared following a procedure similar to that for **7a**. A yellow powder was obtained. Yield: 92%. Anal. Calcd. for C₃₈H₄₁PdClF₆N₅O₃P: C, 50.57, H, 4.58, N, 7.76; Found: C, 50.50, H, 4.72, N, 7.68. H¹ NMR (300 MHz, *d*₆-DMSO, 25 °C): δ = 8.10 (m, 4 H), 7.81 (m, 4 H), 7.15–7.54 (m, 10 H), 5.77 (s, 4 H), 4.54–4.85 (m, 4 H), 3.70–3.92 (m, 8 H), 3.19–0.3.67 (m, 4 H), 2.01 (s, 3 H).

¹³C NMR (75 MHz, *d*₆-DMSO, 25 °C): δ = 165.09 (NCN), 133.86, 131.75, 131.20, 129.68, 129.13, 128.33, 127.40, 126.55 (Ar-C), 125.98, 124.34, 123.97, 123.57(im-C), 119.1 (MeCN), 70.95, 70.38, 69.9, 69.8, (OCH₂) 51.87(ArCH₂N), 48.12 (N-CH₂), 1.2 (MeCN) ppm.

1,1'-[Oxybis(2,1-ethanediylloxy-2,1-ethanediyl)]bis[3-(9-anthracenylmethyl)imidazol-2-ylidene]palladium hexafluorophosphate (**9b**)

The complex was prepared following a procedure similar to that for **7a**. A yellow powder was obtained. Yield: 92%. Anal. Calcd. for C₄₆H₄₅PdClF₆N₅O₃P: C, 55.10, H, 4.52, N, 6.98; Found: C, 54.92, H, 4.46, N, 7.16. H¹ NMR (300 MHz, *d*₆-DMSO, 25 °C): δ = 8.76 (s, 2 H), 8.63 (d, ³J_{H,H} = 7.8 Hz, 4 H), 8.14 (d, ³J_{H,H} = 8.2 Hz, 4 H), 7.46–7.68 (m, 10 H), 6.88 (d, ³J_{H,H} = 13.8 Hz, 2 H), 6.51 (d, ³J_{H,H} = 14.8 Hz, 2 H), 6.42 (s, 2 H), 4.70–4.78 (m, 4 H), 4.09–4.14 (m, 4 H), 3.18–3.70 (m, 8 H), 2.07 (s, 3 H) ppm. ¹³C NMR (75 MHz, *d*₆-DMSO, 25 °C): δ = 165.2 (NCN), 131.62, 131.43, 130.30, 129.92, 128.21, 126.15 (Ar-C), 124.97, 124.69, 124.43, 122.11(im-C), 117.1 (MeCN), 70.89, 70.12, 69.75, 69.6 (OCH₂), 51.64(ArCH₂N), 50.48 (N-CH₂), 1.2 (MeCN) ppm.

Catalysis

General procedure for the Suzuki coupling reactions

In a typical run, a mixture of aryl bromides (0.5 mmol), phenylboronic acid (0.6 mmol), KOH (1.5 mmol) and 1% mmol of catalyst in 3 mL of 1,4-dioxane was stirred at 75 °C for 5 h under nitrogen. Water was added to the reaction mixture, the organic layer was extracted with diethyl ether, dried over magnesium sulfate, and the solvent was removed completely under high vacuum to give a crude product. The pure product was isolated by column chromatography on silica.

General procedure for the Heck coupling reactions

In a typical run, a mixture of aryl bromides (0.5 mmol), styrene (0.6 mmol), KOH (1.5 mmol) and 1% mmol of catalyst in 3 mL of DMF were stirred at 120 °C for 5 h under nitrogen. Water was added to the reaction mixture, the organic layer was extracted with diethyl ether, dried over magnesium sulfate, and the solvent was removed completely under high vacuum to give a crude product. The pure product was isolated by column chromatography on silica.

X-ray structure crystallography

Crystals of **7a** suitable for X-ray diffraction analysis were grown from layering a saturated CH₃CN and chlorobenzene solution with diethyl ether. Suitable crystals of **7a** were mounted on a glass fiber in a random orientation. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. Data collection was performed at room temperature on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo-K α radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters and included in structure factor calculations.

Supplementary material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center: CCDC-714292 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, <http://www.ccdc.cam.ac.uk/datarequest/cif>.

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