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A new class of *o*-hydroxyaryl-substituted *N*-heterocyclic carbene ligands and their complexes with palladium

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Abstract

A facile synthesis of *o*-hydroxyaryl-substituted *N*-heterocyclic carbene ligands and their complexes with palladium is presented. This kind of salicylaldimine-like NHC ligands expands the class of available NHC ligands for organometallic catalysts.

Keywords: *o*-Hydroxyaryl-substituted *N*-heterocyclic carbene; Palladium; Crystal structure; Suzuki–Miyaura coupling

1. Introduction

Since the isolation of the free *N*-heterocyclic carbene (NHC) by Arduengo and co-workers firstly in 1991, NHC ligands have been used extensively in organometallic and catalytic reactions [1]. As neutral two-electron-donor ligands, NHCs are strong σ-donors and weak π-acceptors [1d–3]. This feature provides their metal complexes quite different electronic properties and reactivities compared with the traditional neutral ligands such as phosphines [1d]. Some NHC complexes show enhanced activities in catalytic reactions than their analogues [1e,4,5]. Concerning the structural feature, it is easy to change the steric and electronic feature through changing the substituents on the nitrogen atoms. This provides a way to control the reaction and catalytic activities of their metal complexes.

Recently much research effort has been devoted to the study of [C, O] chelating NHC ligands. There are three types of framework being able to provide an [C, O] chelating (Chart 1). The bonding between the NHC and metal can be enhanced by alkoxide or phenoxide as a sidearm through the incorporation of chelating anionic oxygen, such as **A**. Some metal complexes bearing such ligands were synthesized, characterized, and applied in catalysis [6]. Framework **B** provides another interesting structure of [C, O] chelating [7]. Unfortunately, this kind of NHC enolate metal complexes is unstable to electrophiles [7a], which limits their applications. Framework **C** is the most interesting type of [C, O] chelating. This kind of *o*-hydroxyaryl-substituted NHC ligands would be analogue of the salicylaldimine framework, a common motif in organometallic chemistry [8,9a]. But the reports of such *o*-hydroxyaryl-substituted NHCs are really rare [9] due to the difficulty in the synthesis of the ligands. Hoveyda et al. reported binaphthol substituted NHCs and their metal complexes [10]. Grubbs et al. reported the synthesis of a class of *o*-hydroxyaryl substituted saturated NHCs and their Pd and Ni complexes [9]. However, the synthesis of these ligands is somewhat lengthy. Here we report a facile synthesis of *o*-hydroxyaryl substituted unsaturated NHCs and their Pd allylic complexes.

2. Results and discussion

In 1981, Tashiro et al. discovered that 4-bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one (**1**) reacted with nucleophilic reagent such as pyridine afforded an unexpected *o*-substituted phenol (Scheme 1) [11]. Then they expanded

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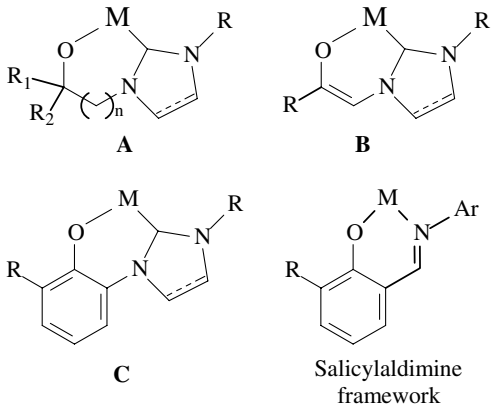
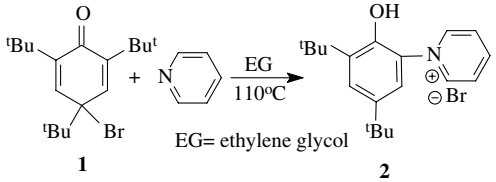


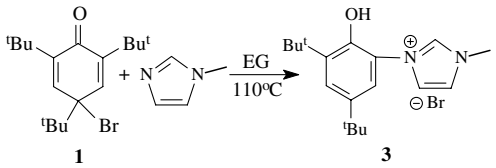
Chart 1.



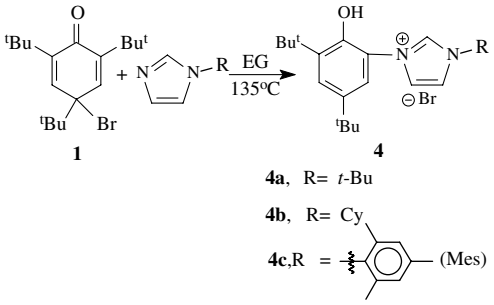
Scheme 1.

the reactant to 1-methylimidazole, and the *o*-hydroxyaryl-substituted imidazolium salt **3** was achieved in moderate yield (35%) (Scheme 2) [12]. However, since then there is no report on the synthesis of the ligands with other *N*-substituted imidazoles and their metal complexes. So we synthesized a series of *o*-hydroxyaryl substituted imidazolium salts **4** from **1** and different *N*-substituted imidazoles using the similar method (Scheme 3).

The reactions were carried out in an argon atmosphere at 135 °C. *N*-Substituted imidazole, ethylene glycol and **1** were added in a molar ratio of 2:1:1 for higher yield. Different to 1-methylimidazole, high reaction temperature (135 °C) is necessary for the formation of **4**, possibly due to the bulky substituents at imidazole of **4**. The yields were lower than that with the less steric reactant *N*-methyl imidazole. The major side products were 2,4,6-tri-*tert*-butylphenol (around 30–40%), acidified *N*-substituted imidazoles (around 20%) and 2-(1,3,5-tri-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-oxy)ethanol (around 10%) [11,12]. The yield with 1-2,6-di-isopropylphenylimidazole was too low to isolate the objective compound. Although the yield of this reaction is somewhat low, the routine is simple and purification is easy, and it can be used for the synthesis of com-



Scheme 2.



Scheme 3.

pounds **4** in large scale. The compounds **4** are soluble in CH_2Cl_2, $CHCl_3$, methanol and insoluble in hexane and diethyl ether. All the ^1H NMR spectra show a singlet at 9–10 ppm for the imidazolium proton (9.50 for **4a**, 9.48 for **4b**, and 10.06 for **4c**), two singlets for the phenyl protons, two doublets for the imidazole protons, and two singlets for the *tert*-butyl groups at the aryl ring, but no the signal of phenol proton. It agrees with the spectra of **3** [12] and other known imidazolium salts [12]. Compared with their saturated analogues reported by Grubbs, the resonances for imidazolium protons are shifted downfield obviously, in consistent with the trend between the diaryl imidazolium salts and their saturated analogues [13]. All the Mass spectra of **4** show the cationic peaks of $[M^+-Br]$. The molecular structure of **4b** was further confirmed by single crystal X-ray diffraction analysis (Fig. 1).

The NHC precursors **4** were deprotonated with 2 equiv of *n*-BuLi in THF at room temperature, and then further reacted with $[(allyl)PdCl]_2$ to give the complexes **5a**–**c** (Scheme 4). All three complexes are air stable. Compared with other known NHC allylic palladium complexes, complexes **5a**–**c** are more thermal stable with higher decomposition temperatures [14]. This may due to the rigidity of the chelating ligands, which prevent the reductive elimination [15].

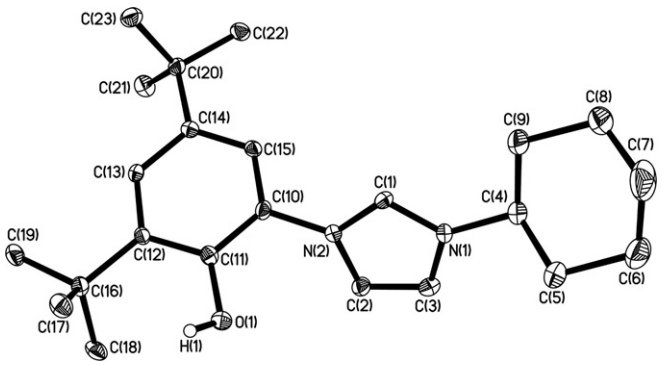
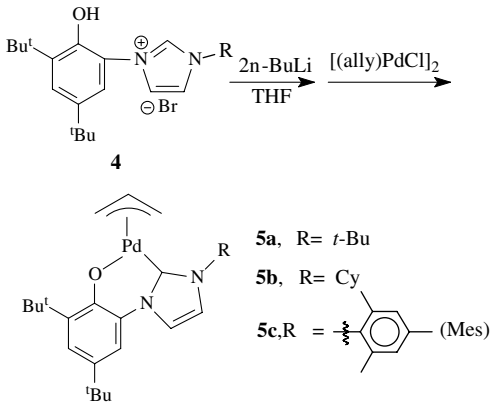


Fig. 1. Molecular structure of **4b**, showing one of the two crystallographically independent molecules in the unit cell. Selected bond lengths (Å) and angles (°): O(1)–C(11) 1.365(6), N(1)–C(1) 1.345(6), N(1)–C(3) 1.380(7), N(1)–C(4) 1.474(7), N(2)–C(1) 1.325(7), N(2)–C(2) 1.379(6), N(2)–C(10) 1.445(6), C(2)–C(3) 1.360(7), C(1)–N(1)–C(4) 127.6(5), C(1)–N(2)–C(10) 125.1(4), N(2)–C(1)–N(1) 108.7(4).



Scheme 4.

The NMR spectra of **5a**–**c** show five proton and three carbon distinct resonances for the allyl ligand, in agreement with asymmetric structures of the complexes [16]. The signals of carbene carbons are typical singlets at around 180 ppm (175.4 for **5a**, 175.6 for **5b**, and 178.6 for **5c**). The chemical shifts are very similar with the known η^3-allylic palladium Schiff base complexes [17] and η^3-allylic palladium NHC halide complexes [5b,14]. The molecular structure of **5b** was also determined by single crystal X-ray diffraction analysis (Fig. 2). Similar to the other (allyl)Pd(NHC) complexes [5b,14], a square-planar coordination geometry is observed. The allyl carbon *trans* to the carbene also shows significant lengthening (0.106 Å) relative to the allyl carbon *trans* to the phenolate. But the bonding between the allyl and palladium [Pd–C(allyl): 2.076(12), 2.131(3), 2.182(12) Å] in **5b** is shorter, while the Pd–C(carbene) [2.033(2) Å] and Pd–O [2.0819(17) Å] bonds are slightly longer than that in the analogous allyl palladium NHC enolate complex [Pd–C(allyl): 2.113(4), 2.133(5), 2.204(4) Å; Pd–C(carbene): 2.022(4) Å; Pd–O: 2.062(3) Å] [5b]. In comparison with the carbene precursor **4b**, the notable feature of **5b** is the shortened C–O bond [from 1.365(6) to 1.322(3) Å] and the lengthened and averaged C(carbene)–N bonds [from 1.325(7), 1.345(6) to 1.363(3), 1.359(3) Å], indicating the strong complexation between Pd and the [C, O] chelating NHC ligand.

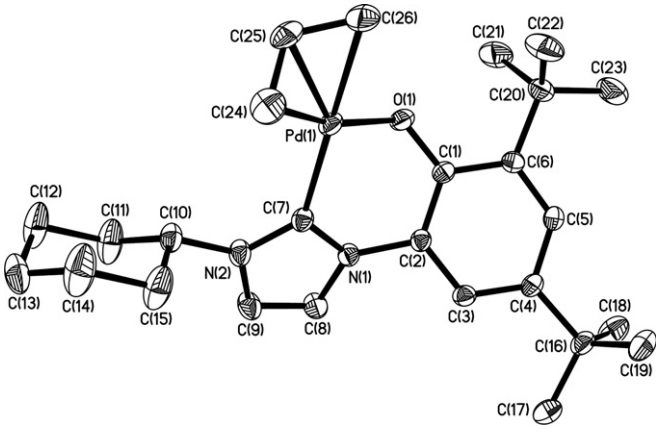
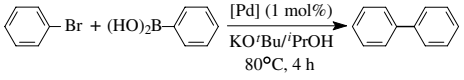


Fig. 2. Molecular structure of **5b**. Selected bond lengths (Å) and angles (°): O(1)–C(1) 1.322(3), N(1)–C(2) 1.438(3), N(1)–C(7) 1.363(3), N(1)–C(8) 1.384(3), N(2)–C(7) 1.359(3), N(2)–C(9) 1.385(3), N(2)–C(10) 1.468(3), C(8)–C(9) 1.338(3), Pd(1)–C(7) 2.033(2), Pd(1)–O(1) 2.0819(17), Pd(1)–C(24) 2.076(12), Pd(1)–C(25) 2.131(3), Pd(1)–C(26) 2.182(12), C(24)–C(25) 1.385(10), C(25)–C(26) 1.388(9), C(24)–Pd(1)–C(26) 68.1(3), C(7)–Pd(1)–O(1) 85.78(8), C(1)–O(1)–Pd(1) 118.58(14), O(1)–C(1)–C(2) 122.1(2), C(1)–C(2)–N(1) 119.36(19), C(7)–N(1)–C(2) 126.08(19), N(1)–C(7)–Pd(1) 120.96(16), N(2)–C(7)–N(1) 104.61(19), C(7)–N(2)–C(10) 124.5(2), C(24)–C(25)–C(26) 118.7(7).

It is well known that palladium complexes are excellent catalysts for Suzuki–Miyaura coupling [18] and Buchward–Hartwig amination [19]. Some of the *N*-heterocyclic carbene allylic palladium complexes were found with extremely high activities [14,20]. Introduction of the chelating anionic oxygen to the NHC allylic palladium complexes may lead to some different results. So a series of Suzuki–Miyaura coupling reactions was tried with complexes **5a**–**c** as catalysts. Under the typical conditions as for the NHC allylic palladium catalysts, bromobenzene could be coupled with phenyl boronic acid in the presence of 1.1 equiv of KO^{t}Bu using 1 mol% of **5** in 1 mL of ^{i}PrOH at 80 °C (Table 1). All reactions nearly finished in 4 h. This indicates that complexes **5** are efficient catalysts for Suzuki–Miyaura coupling reaction. Similar to the NHC allylic palladium catalysts [14b], the aryl substituted complex **5c** is more effective than the alkyl substituted analogues **5a** and **5b**. This can be attributed to the poor stability of the [(NHC)Pd(0)] intermediate for **5a** and **5b**, because the catalyst decomposition (Pd black formation) was observed in the cases of **5a** and **5b**. Addition of PPh_3 may stabilize the [(NHC)Pd(0)] intermediate and increase the yield. The coupling of different substrates with phenyl boronic acid was also studied with **5c** as catalyst (Table 2). For aryl bromide and the active aryl chloride, good results were obtained. But for chlorobenzene only poor yield was obtained. Addition of PPh_3 could promote the reaction, but the yield was still low. This indicates that this

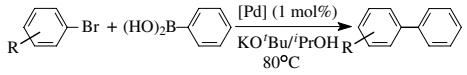
Table 1
Effect of the substitution at the imidazolyl moiety on precatalyst and PPh_3 performance in the Suzuki–Miyaura coupling of a simple substrate[a]

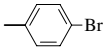
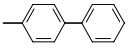
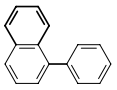
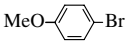
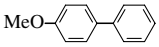
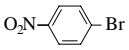
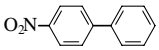
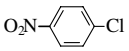
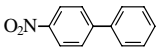
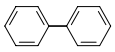
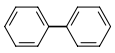


Entry	[Pd]	Yield[b] (%)
1	**5a**	81[c]
2	**5a** + PPh_3[d]	>99
3	**5b**	82[c]
4	**5b** + PPh_3	>99
5	**5c**	>99
6	**5c** + PPh_3	>99

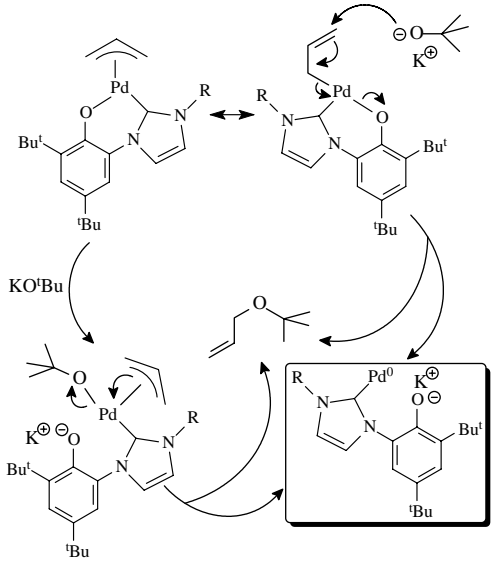
[a] Reaction conditions: phenyl bromide (1 mmol), boronic acid (1.5 mmol), [Pd] (1 mol %), KO^{t}Bu (1.1 mmol), tech grade ^{i}PrOH (1 mL).
[b] Isolated yield, average of two runs.
[c] Catalyst decomposed.
[d] PPh_3 (1 mmol).

Table 2
Suzuki reaction of aryl halides catalyzed by **5c**[a]



Entry	ArX	[Pd]	Product	Time (h)	Yield[b] (%)
1		**5c**		4	96
2		**5c**		4	89
3		**5c**		4	>99
4		**5c**		2	>99[c]
5		**5c**		4	98
6		**5c**		6	14[d]
7		**5c** + PPh_3[e]		6	26[d]

[a] Reaction conditions: phenyl bromide (1 mmol), boronic acid (1.5 mmol), [Pd] (1 mol%), KO^{t}Bu (1.1 mmol), tech grade ^{i}PrOH (1 mL).
[b] Isolated yield, average of two runs.
[c] At room temperature.
[d] Catalyst decomposed.
[e] PPh_3 (1 mmol).



Scheme 5.

kind of *o*-hydroxyaryl-substituted NHC ligands is not advantaged for Suzuki–Miyaura coupling reaction, in comparison with the NHC allylic palladium catalysts.

In the most recognized mechanism of Suzuki–Miyaura coupling reaction catalyzed by (allyl)Pd(NHC)Cl, the activation of the Pd center may occur through a nucleophilic attack at the allyl moiety or through a chloride/alkoxide σ-metathesis followed by reductive elimination, liberating a [(NHC)Pd(0)] species [16b,20,21] (Scheme 5). In our cases, the chelating anionic oxygen is a much weaker leaving group than chloride. So the activation process is harder than that for (allyl)Pd(NHC)Cl and leads to the low yield.

3. Conclusions

In conclusion, a facile protocol for the synthesis of *o*-hydroxyaryl substituted carbene is presented. Allylic palladium complexes **5a–c** bearing such ligands were synthesized and used as efficient catalysts for Suzuki–Miyaura coupling reaction of aryl bromide.

4. Experimental

4.1. General procedures and starting materials

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. All solvents were distilled from appropriate drying agents under argon before use. ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN 400 instrument. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Allyl palladium chloride dimer [22], 1-substituted imidazoles [23] and **1** [24] were prepared according to the literature methods.

4.2. General procedures for preparation of *o*-hydroxyaryl substituted imidazolium salts *4a–c*

4-Bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one (6.83 g, 20 mmol), ethylene glycol (1.24 g, 20 mmol), and *N*-substituted imidazole (40 mmol) were heated in an oil bath at 135 °C for 8 h. Then 50 mL of HBr aqueous solution (3 N) was added and stirred violently. After filtration, the solid was washed with water (3 × 10 mL) and hexane (3 × 20 mL) to give the *o*-hydroxyaryl substituted imidazolium salts **4** as white powder. They were pure enough for ^{1}H NMR Spectra characterization. Recrystallization from CH_2Cl_2/hexane made the further purification for element analysis.

4.2.1. Compound *4a* (*R* = *t*-Bu)

Yield 19%, mp: 255–256 °C. Anal. Calc. for $C_{21}H_{33}N_2OBr$: C, 61.61; H, 8.12; N, 6.84. Found: C, 61.29; H, 8.01; N, 6.35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H, $C_{carbene}H$), 7.55 (s, 1H, Ar–*H*), 7.46 (d, 1H, im–C*H*, $J = 2.29$ Hz), 7.38 (s, 1H, Ar–*H*), 7.01 (d, 1H, im–C*H*, $J = 2.29$ Hz), 1.81 (s, 9H, C(C*H*)$_3$), 1.46 (s, 9H,

C(CH)$_3$), 1.30 (s, 9H, C(CH)$_3$). MS (SCI): $m/z = 329$ (M^+−Br).

*4.2.2. Compound **4b** (R = Cy)*

Yield 18%, mp: 236–237 °C. Anal. Calc. for $C_{23}H_{35}N_2OBr$: C, 63.44; H, 8.10; N, 6.43. Found: C, 63.49; H, 8.54; N, 6.92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H, $C_{carbene}H$), 7.52 (s, 1H, Ar–H), 7.46 (d, 1H, im–CH, $J = 2.36$ Hz), 7.37 (s, 1H, Ar–H), 7.01 (d, 1H, im–CH, $J = 2.36$ Hz), 4.38 (m, 1H, NCH(CH$_2$)$_5$), 2.48–1.65 (m, 10H, (CH_2)$_5$), 1.44 (s, 9H, C(CH)$_3$), 1.30 (s, 9H, C(CH)$_3$). MS (SCI): $m/z = 355$ (M^+−Br).

*4.2.3. Compound **4c** (R = Mes)*

Yield 20% yield, mp: 278–279 °C. Anal. Calc. for $C_{26}H_{35}N_2OBr$: C, 66.23; H, 7.48; N, 5.94. Found: C, 66.17; H, 7.86; N, 6.15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H, $C_{carbene}H$), 7.65 (m, 1H, Ar–H), 7.52 (d, 1H, im–CH, $J = 2.10$ Hz), 7.31 (m, 1H, Ar–H), 7.11 (d, 1H, im–CH, $J = 2.10$ Hz), 7.04 (s, 2H, Ar–H), 2.35 (s, 3H, Ar–CH_3), 2.26 (s, 6H, Ar–CH_3), 1.49 (s, 9H, C(CH)$_3$), 1.34 (s, 9H, C(CH)$_3$). MS (SCI): $m/z = 391$ (M^+−Br).

4.3. General procedures for preparation of chelating N-heterocyclic carbene palladium complexes **5a–c**

A solution of *n*-BuLi (1.7 M, 2.0 mmol) in hexane was added to the suspension of imidazolium salt (1.0 mmol) in THF. After stirring for 30 min, [Pd(allyl)Cl]$_2$ (0.18 g, 0.5 mmol) was added and the resulting orange solution was stirred overnight. After removal of solvents in vacuum, the residue was extracted with CH_2Cl_2 and filtered through Celite. Removal of CH_2Cl_2 gave the object complex in high yield.

*4.3.1. Compound **5a** (R = t-Bu)*

Yield 90%, mp: >250 °C (dec). Anal. Calc. for $C_{24}H_{36}N_2OPd$: C, 60.69; H, 7.64; N, 5.90. Found: C, 60.51; H, 7.41; N, 5.84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 2H, Ar–H), 7.18 (d, 1H, im–CH,$J = 2.58$ Hz), 7.02 (d, 1H, im–CH,$J = 2.58$ Hz), 5.32 (m, 1H, $C_{ally}H$), 4.25 (dd, 1H, $C_{ally}H$,$J = 2.05$, 7.50 Hz), 3.28–3.20 (m, 2H, $C_{ally}H$), 2.35 (d, 1H, $C_{ally}H$,$J = 11.8$ Hz), 1.76 (s, 9H, C(CH)$_3$), 1.48 (s, 9H, C(CH)$_3$), 1.32 (s, 9H, C(CH)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ175.4, 157.6, 140.6, 134.4, 132.1, 122.3, 118.9, 118.4, 116.3, 114.6, 69.8, 57.8, 48.0, 35.6, 34.0, 31.8, 31.5, 29.8.

*4.3.2. Compound **5b** (R = Cy)*

Yield 90%, mp: >250 °C (dec). Anal. Calc. for $C_{26}H_{38}N_2OPd$: C, 62.33; H, 7.64; N, 5.59. Found: C, 62.21; H, 7.68; N, 5.51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 1H, Ar–H, $J = 1.73$ Hz), 7.18 (d, 1H, im–CH, $J = 2.44$ Hz), 7.08 (d, 1H, Ar–CH, $J = 1.84$ Hz), 7.03 (d, 1H, im–CH, $J = 2.44$ Hz), 5.26 (m, 1H, $C_{ally}H$), 4.36 (m, 1H, NCH(CH$_2$)$_5$), 4.21 (d, 1H, $C_{ally}H$, $J = 7.47$ Hz), 3.30 (d, 1H, $C_{ally}H$, $J = 13.7$ Hz), 3.20 (d, 1H, $C_{ally}H$, $J = 6.56$ Hz), 2.29 (d, 1H, $C_{ally}H$, $J = 11.7$ Hz), 2.18–1.52 (m, 10H, (CH_2)$_5$), 1.49 (s, 9H, C(CH)$_3$), 1.31 (s, 9H, C(CH)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ175.6, 157.1, 141.1, 134.4, 130.1, 121.9, 119.4, 116.8, 115.6, 115.0, 69.9, 60.4, 41.6, 35.7, 34.1, 34.0, 31.8, 29.6, 25.7, 25.3.

*4.3.3. Compound **5c** (R = Mes)*

Yield 95%, mp: 209–210 °C (dec). Anal. Calc. for $C_{29}H_{38}N_2OPd$: C, 64.86; H, 7.13; N, 5.22. Found: C, 64.81; H, 7.13; N, 5.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H, Ar–H), 7.23 (m, 1H, im–CH,), 7.14 (m, 1H, im–CH,), 7.00 (s, 1H, Ar–H), 6.97 (s, 2H, Ar–H), 4.96 (m, 1H, $C_{ally}H$), 4.04 (d, 1H, $C_{ally}H$, $J = 7.48$ Hz), 3.06 (d, 1H, $C_{ally}H$, $J = 13.6$ Hz), 2.36 (s, 3H, Ar–CH_3), 2.19 (d, 1H, $C_{ally}H$, $J = 5.00$ Hz), 2.10 (s, 3H, Ar–CH_3), 2.02 (s, 3H, Ar–CH_3), 1.93 (d, 1H, $C_{ally}H$, $J = 6.01$ Hz), 1.50 (s, 9H, C(CH)$_3$), 1.34 (s, 9H, C(CH)$_3$); ^{13}C NMR (400 MHz, $CDCl_3$): δ178.6, 157.2, 141.4, 139.0, 137.2, 135.8, 135.6, 134.4, 129.4, 128.7, 122.2, 121.2, 119.2, 115.9, 115.2, 68.4, 42.1, 35.8, 34.1, 31.8, 29.7, 21.1, 18.0, 17.9.

4.4. General procedure of Suzuki–Miyaura coupling reactions

To a Schlenk bottle with a magnetic stir bar and a septum were added in turn catalyst (1 mmol%), potassium *tert*-butoxide (1.1 mmol, 124 mg), boronic acid (1.5 mmol, 183 mg) and aryl halide (1 mmol, if solid). Then the system

Table 3
Crystal data and summary of X-ray data collection for **4b** and **5b**

	4b · 0.75H_2O	**5b**
Formula	$C_{23}H_{36.5}BrN_2O_{1.75}$	$C_{26}H_{38}N_2OPd$
Fw	448.95	500.98
T (K)	113(2) K	294(2)
λ (Å)	0.71070	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P_12_1/a_1	$P\bar{1}$
a (Å)	11.176(2)	9.8536(13)
b (Å)	28.222(5)	9.9100(13)
c (Å)	14.987(3)	14.8527(18)
α (°)	90	82.761(2)
β (°)	90.392(3)	86.366(2)
γ (°)	90	60.250(2)
V (Å^3)	4726.9(15)	1249.2(3)
Z	8	2
D_{calc} (g cm^{-3})	1.262	1.332
μ (mm^{-1})	1.757	0.761
F(000)	1900	524
Crystal size (mm)	0.32 × 0.20 × 0.10	0.28 × 0.20 × 0.12
θ Range (°)	1.96–25.00	2.38–26.36
Number of reflections collected	35897	7103
Number of independent reflections/R_{int}	8309/0.1359	5041/0.0164
Number of parameters	520	305
Goodness-of-fit on F^2	1.071	1.028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0722, 0.1791	0.0285, 0.0711
R_1, wR_2 (all data)	0.0915, 0.1929	0.0339, 0.0747

was degassed and charged with argon three times. Degassed aryl halide (1 mmol, if liquid) and *i*-PrOH (technical grade, 1 mL) were injected through the septum. The mixture was stirred at room temperature for 5 min and it turned to a clear solution. Then the mixture was heated at 80 °C. When the reaction reached completion, water was added, then the organic layer was extracted with diethyl ether, dried over sodium sulfate. Removal of solvents in vacuo gave the product. When necessary the product was further purified by chromatography.

4.5. Crystallographic studies

Single crystals of **4b** and **5b** suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane solution. Data collection was performed on Rigaku 007 with Saturn 70 CCD (for **4b**) or Bruker Smart 1000 (for **5b**) diffractometer, using graphite-monochromated Mo Kα radiation (ω–2θ scans). Semi-empirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 3.

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Appendix A. Supplementary material

CCDC 634034 and 631539 contain the supplementary crystallographic data for **4b** and **5b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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