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Non-symmetrically substituted di-*N*-heterocyclic carbene palladium(II) complexes: Synthesis, structure and catalytic activity

Tressia A.P. Paulose [a], Jeremy A. Olson [a], J. Wilson Quail [b], Stephen R. Foley [a,*]

[a] Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan, Canada S7N 5C9
[b] Saskatchewan Structural Sciences Centre, 110 Science Place, Saskatoon, Saskatchewan, Canada S7N 5C9

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ABSTRACT

The synthesis and characterization of non-symmetric di-*N*-heterocyclic carbene (diNHC) silver(I) and palladium(II) complexes are described. The activity of the Pd(II) complexes in the Suzuki–Miyaura coupling reaction of bulky substrates was investigated. This synthetic route represents a possible general pathway into a wide variety of non-symmetrically substituted diNHC ligands.

1. Introduction

N-Heterocyclic carbenes (NHCs) have received considerable attention as ligands in transition metal coordination chemistry which has resulted in the synthesis of a wide variety of stable metal–carbene complexes with numerous applications as catalysts for organic transformations [1]. Chelating di-*N*-heterocyclic carbene ligands (diNHCs) in particular are expected to provide increased entropic stability to a metal center and consequently many reports have emerged in recent years concerning *cis*-chelating bidentate alkane-bridged diNHCs [2].

While the preparation of diverse symmetrically substituted diNHC ligands have been reported, there are no examples of non-symmetrically substituted diNHC ligands in the literature where $R \neq R'$ (Fig. 1) [3]. There is, however, one example of a non-symmetric diNHC ligand employing variations of Crabtree's abnormal NHC ligand for applications in iridium chemistry [4]. Here, we report the synthesis of non-symmetrically substituted ethylene-bridged diimidazolium salts and their corresponding diNHC palladium(II) complexes. Given the effectiveness of reported (diNHC)Pd(II) complexes in C–C coupling reactions [1–3], preliminary investigations into the activity of these complexes in the Suzuki–Miyaura coupling reaction of bulky substrates were performed.

2. Results and discussion

2.1. Synthesis of ligands

The key step in the synthesis of non-symmetric imidazolium salts **3a,b** is isolation of the bromoethylimidazolium bromide precursor **2a,b** which is easily synthesized from an *N*-substituted imidazole and excess 1,2-dibromoethane (Scheme 1). The synthesis of **2a** has been previously reported [5]. The second step simply involves reaction of **2a,b** with another equivalent of a *N*-substituted imidazole in toluene resulting in the non-symmetrically substituted diimidazolium salts **3a,b** in 90% yield. Preliminary results suggest this is a general route to non-symmetric diNHCs provided the bromoethylimidazolium bromide precursors can be isolated. The ^{1}H NMR spectra of **3** in DMSO-d_6 exhibit two distinct resonances at 9.32 and 9.17 ppm for **3a** and at 9.25 and 9.12 ppm for **3b** for the two NC*H*N protons on the two ethylene-bridged imidazolium rings. There are also four distinct resonances for the protons on the remaining four carbons of the two imidazolium rings. Single crystals of **3a** were obtained by slow diffusion of ether into a concentrated solution in DMF. The crystal structure of **3a** shows an anti conformation of the imidazolium units about the C_2 bridge with the imidazolium units oriented in opposite directions (Fig. 2 and Table 1).

2.2. Synthesis of (diNHC)Ag(I) and (diNHC)Pd(II) complexes

Complexes **5a,b** were synthesized via a transmetallation route using (diNHC)Ag(I) complexes (Scheme 1). The advantage of using

* Corresponding author. Tel.: +1 306 966 2960; fax: +1 306 966 4730.
E-mail address: stephen.foley@usask.ca (S.R. Foley).

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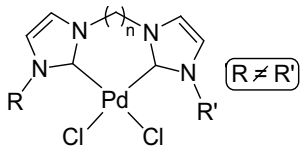
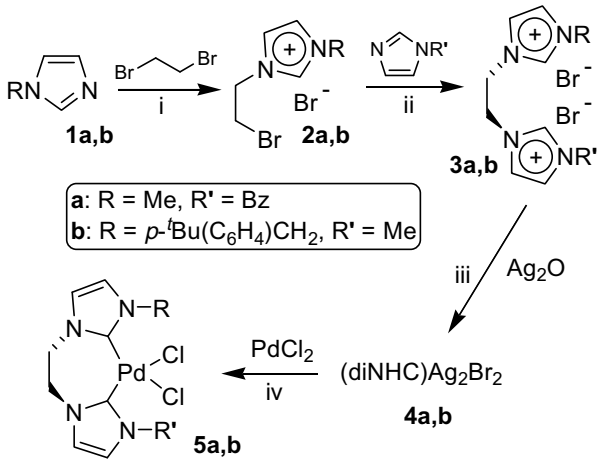


Fig. 1. Non-symmetrically substituted (diNHC)$PdCl_2$.



Scheme 1. Synthesis of non-symmetric (diNHC)$PdCl_2$ complexes. Conditions: (i) neat, 2 d, 80 °C; (ii) toluene, 3 d, 80–150 °C; (iii) DCM, 2 h, rt and (iv) DMF, 24 h, 90 °C.

Table 1
Crystal data and refinement parameters for compounds **3a**, **5a** and **5b-DMF**

	3a	**5a**	**5b-DMF**
Formula	$C_{16}H_{20}Br_2N_4$	$C_{16}H_{18}Cl_2N_4Pd$	$C_{23}H_{33}Cl_2N_5OPd$
Formula weight	428.18	443.64	572.84
Color	Colorless	Pale yellow	Colorless
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	27.1963(15)	8.3715(2)	13.6740(9)
b (Å)	5.1619(3)	17.8428(4)	14.0256(9)
c (Å)	12.5926(5)	14.3790(4)	13.3806(11)
β (°)	91.922(3)	124.492(2)	94.680(4)
Z	4	4	4
ρ_{calc} (mg m^{-3})	1.610	1.665	1.488
Temperature, K	173(2)	173(2)	173(2)
$F(000)$	856	888	1176
θ Range (°)	3.00–23.25	2.69–27.46	2.99–25.35
Reflections collected/unique	12024/2398	25351/4040	19094/4659
R_{int}	0.1221	0.0772	0.1088
Final R_1 ($I > 2\sigma I$)	R_1 = 0.0943, wR_2 = 0.1814	R_1 = 0.0552, wR_2 = 0.1412	R_1 = 0.0600, wR_2 = 0.1333
R_1 (all data)	R_1 = 0.1219, wR_2 = 0.1955	R_1 = 0.0727, wR_2 = 0.1550	R_1 = 0.0848, wR_2 = 0.1473

(diNHC)Ag(I) complexes as carbene transfer reagents include simple preparation directly from the imidazolium salt and ease of handling due to their stability in air [6]. (DiNHC)Ag(I) complexes **4a,b** were synthesized by the reaction of the diimidazolium salt precursors **3a,b** with an equivalent amount of Ag_2O according to established procedures [3c]. The ^{1}H NMR spectra of **4a,b** (DMSO-d_6) show the absence of any signal in the 8–10 ppm region indicating the successful deprotonation of the carbenic protons in **3a,b**. The bridging ethylene protons in **4a,b** now appear as two multiplets each integrating for two protons compared to the singlet obtained for **3a,b**. The ^{13}C NMR spectra of **4a,b** show the appearance of two resonances at 181 and 180 ppm which is characteristic of the two non-symmetric carbenic (NCN) carbons. Elemental analysis is consistent with formation of (diNHC)Ag_2Br_2.

Subsequent reaction of the silver complexes **4a,b** with one equiv. $PdCl_2$ in DMF at 90 °C for 16 h afforded the desired complexes **5a,b** in 50–60% yield. The ^{13}C NMR spectra of **5** show the appearance of two resonances at 156 and 154 ppm for **5a** and at 155 and 154 ppm for **5b** which is again characteristic of the two non-symmetric carbenic carbons. The ethylene bridge and methylene protons of the benzyl moiety exhibit broad resonances in the ^{1}H NMR spectra which is likely due to the inherent fluxionality of the seven-membered palladacycle. This phenomenon has been previously observed in reported (diNHC)Pd(II) complexes [3b]. Complexes **5a,b** are air and moisture stable and can be crystallized by slow diffusion of ether into a concentrated solution of the sample in DMF. The solid state structures of complexes **5a,b** were determined by single-crystal X-ray diffraction, which showed the palladium in a distorted square planar geometry (Figs. 3 and 4 and Table 1). Complex **5b** co-crystallized with one molecule of DMF. In both structures the palladacycles adopt boat-like confor-

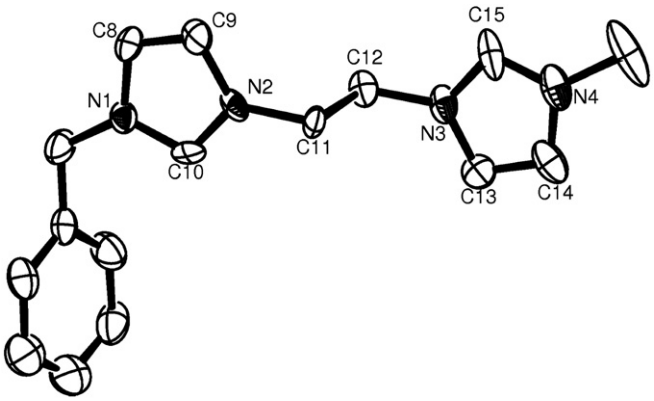


Fig. 2. ORTEP plot of non-symmetrically substituted diimidazolium salt **3a** at the 50% probability level. The hydrogen atoms and bromide anions are omitted for clarity. Selected bond angles (°): N(2)–C(10)–N(1) = 108.4(12), N(4)–C(15)–N(3) = 108.5(16).

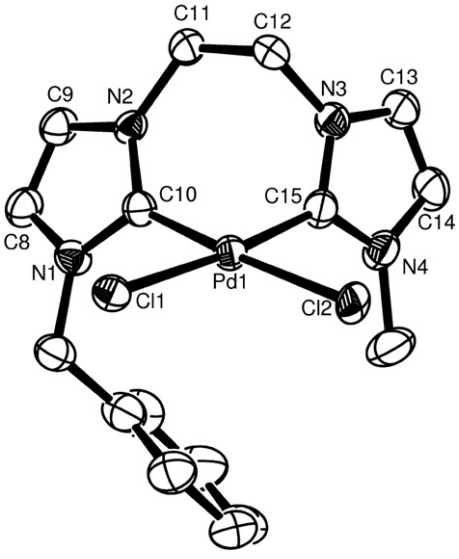


Fig. 3. ORTEP plot of **5a** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(15) = 1.967(5), Pd(1)–C(10) = 1.982(6), C(15)–Pd(1)–C(10) = 86.3(2), N(1)–C(10)–N(2) = 104.9(5), N(4)–C(15)–N(3) = 106.0(5).

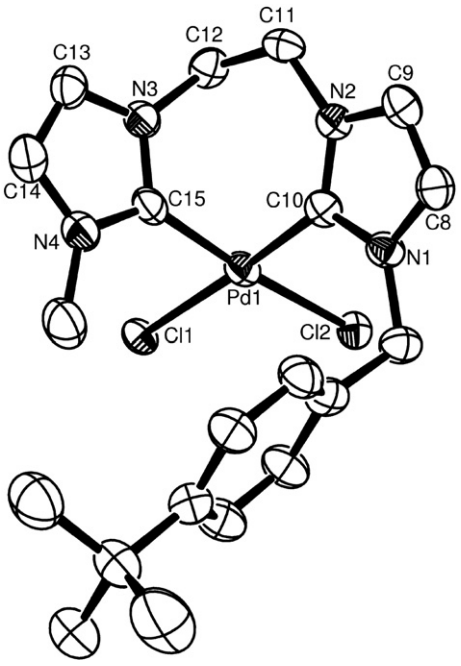


Fig. 4. ORTEP plot of **5b**-**DMF** at the 50% probability level. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(15) = 1.953(6), Pd(1)–C(10) = 1.985(6), C(15)–Pd(1)–C(10) = 85.9(2), N(2)–C(10)–N(1) = 104.5(5), N(3)–C(15)–N(4) = 104.8(5).

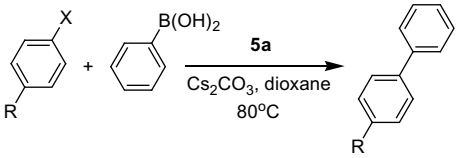
mations where the benzyl moiety of the chelating diNHC ligand is oriented towards the axial face of the palladium center.

2.3. Catalytic activity

The catalytic activity of complex **5a** was investigated in the Suzuki–Miyaura coupling reaction of bulky and non-bulky substrates. In recent years, several powerful systems have been developed for the activation of not only *para*-substituted aryl chlorides [7] but hindered substrates such as *ortho*-substituted aryl halides as shown by Buchwald's group [8]. In our case, excellent yields were obtained in the standard coupling reaction of *para*-substituted aryl bromides with phenyl boronic acid when both activated and deactivated aryl bromides were employed even at very low catalyst loading (Table 2). However, activity significantly decreased when aryl chlorides were employed with no coupling product observed in the presence of deactivated aryl chlorides (entry 5). These results are in contrast to *trans*-$(NHC)_2PdCl_2$ complexes which show high activity for deactivated aryl chlorides under similar conditions [9]. Current state of the art for Suzuki–Miyaura reactions employing NHC complexes of palladium is 0.1 mol% catalyst loading at ambient temperature for deactivated aryl chlorides [10].

Given the recent interest in catalysts that can couple sterically hindered substrates [8], the activity of precatalyst **5a** for the coupling of bulky substrates was investigated (Table 3). High to moderate yields were obtained for mono and di *ortho*-substituted biaryls provided the steric bulk was incorporated on only one of the coupling partners. No coupled product was obtained when both partners were sterically hindered. Attempts to couple 2,4,6-trimethylphenylboronic acid yielded mesitylene as the major product.

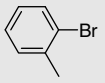
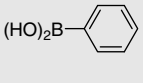
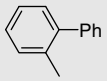
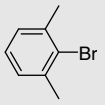
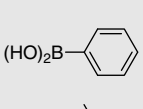
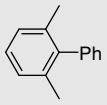
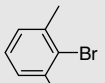
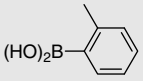
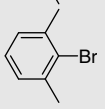
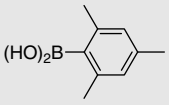
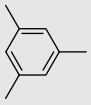
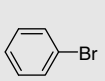
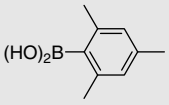
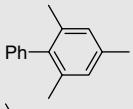
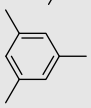
Table 2
Suzuki–Miyaura cross-coupling of aryl halides by complex **5a**[a]



Entry	*R*	*X*	Time (h)	Catalyst (mol%)	Yield (%)[b]	TON[c]
1	COMe	Br	1	0.01	96	9600
2	OMe	Br	6	0.1	95	950
3	COMe	Cl	24	1	37	37
4	H	Cl	24	1	20	20
5	OMe	Cl	24	1	0	0

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), precatalyst **5a**, dioxane (5 mL), 80 °C.
[b] Determined by ^1H NMR based on internal standard dodecahydrotriphenylene.
[c] TON = moles of product per mol of catalyst.

Table 3
Suzuki–Miyaura cross-coupling of bulky aryl halides and aryl boronic acids by complex **5a**[a]

Entry	ArBr	$Ar'B(OH)_2$	Product	Conversion (%)[b]
1				92
2				66
3			No reaction	0
4				80
5				13
				17

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), precatalyst **5a**, dioxane (5 mL), 80 °C, 24 h.
[b] Determined by ^1H NMR based on internal standard dodecahydrotriphenylene.

3. Conclusion

In conclusion, we have synthesized stable non-symmetrically substituted diNHC palladium(II) complexes and have investigated their catalytic activity in the Suzuki–Miyaura coupling reaction of bulky substrates. This synthetic route represents a possible general pathway into a wide variety of non-symmetrically substituted diNHC ligands. These examples of non-symmetrically substituted chelating diNHC ligands can serve in designing NHC ligands with fine-tuned steric and electronic environments around the metal centre.

4. Experimental

4.1. General

Unless otherwise stated, all reactions were performed under N_2 using standard Schlenk techniques or in a N_2-filled drybox. Dichloromethane and THF were dried using a MBraun Solvent Purification System and were stored in a glovebox. All reaction temperatures for catalytic reactions refer to the temperature of

pre-equilibrated sand baths. ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR are reported in ppm in reference to the residual ^{1}H and ^{13}C resonances of $CDCl_3$ (^{1}H: δ 7.24; ^{13}C: δ 77.23) and DMSO-d_6 (^{1}H: δ 2.50; ^{13}C: δ 39.51). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. 1,2-dibromoethane and Ag_2O were purchased from Alfa-Aesar Chemical Company and used as received. Imidazole, *N*-methylimidazole, benzyl bromide, *tert*-butylbenzyl bromide, anhydrous DMF, anhydrous dioxane and NaH were purchased from Sigma–Aldrich Chemical Company and used as received. $PdCl_2$ was obtained from PMO Pty Ltd., Australia. *N*-benzylimidazole [3b] and 1-(2-bromoethyl)-3-methylimidazolium bromide (**2a**) [5] were synthesized according to literature procedures.

4.2. Synthesis of 1-(4-tert-butylbenzyl)imidazole (**1b**)

A Schlenk flask was charged with imidazole (1.85 g, 0.0272 mol) and NaH (2.57 g, 0.107 mol) in THF (50 mL) under dinitrogen at ambient temperature. After 5 min, 4-(*tert*-butyl)benzyl bromide (5.0 mL, 0.0272 mol) was added. The mixture was stirred for 12 h following which the solvent was removed under vacuum. Water (20 mL) and dichloromethane (30 mL) were added to the reaction products and the organic layer was separated. The organic layer was further extracted with water (2 × 20 mL) and the solvent was removed under vacuum to yield **1b** as a pale yellow solid which can be used without further purification. (4.93 g, 85%). ^{1}H NMR ($CDCl_3$): δ 7.52 (s, 1H, NC*H*N), 7.35 (d, J = 8.1, 2H, CH_{Ar}), 7.07 (d, J = 8.1, 2H, CH_{Ar}), 7.06 (s, 1H, CH_{imid}), 6.89 (s, 1H, CH_{imid}), 5.06 (s, 2H, ArCH_2N), 1.29 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): δ 151.59 ($C_{Ar(para)}$), 137.66 (NCHN), 133.44 ($C_{Ar(ipso)}$), 130.00 (*C*H$_{imid}$), 127.26 (*C*H$_{Ar}$), 126.11 (*C*H$_{Ar}$), 119.50 (*C*H$_{imid}$), 50.71 (Ar*C*H$_2$N), 34.82 (*C*(CH$_3$)$_3$), 31.51 (C(*C*H$_3$)$_3$). EI-MS (*m/z*): Calc. for $C_{14}H_{18}N_2$ [M]$^+$: 214. Found: 214.

4.3. Synthesis of 1-(4-tert-butylbenzyl)-3-(2-bromoethyl)imidazolium bromide (**2b**)

A Schlenk flask was charged with **1b** (0.213 g, 0.994 mmol) and 1,2-dibromoethane (10 mL) under dinitrogen. After stirring for 2 d at 80 °C, the resulting white precipitate was isolated and washed with diethyl ether (3 × 10 mL) and dried under vacuum to yield **2b** as a white powder. (0.236 g, 59%). ^{1}H NMR (DMSO-d_6): δ 9.39 (s, 1H, NC*H*N), 7.87 (s, 1H, CH_{imid}), 7.76 (s, 1H, CH_{imid}), 7.44 (d, J = 8.3, 2H, CH_{Ar}), 7.33 (d, J = 8.3, 2H, CH_{Ar}), 5.43 (s, 2H, ArCH_2N), 4.63 (t, J = 5.8, 2H, BrCH_2CH$_2$N), 3.96 (t, J = 5.8, 2H, BrCH$_2$CH_2N), 1.26 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 151.29 ($C_{Ar(para)}$), 136.61 (NCHN), 131.81 ($C_{Ar(ipso)}$), 127.95 (*C*H$_{Ar}$), 125.75 (CH$_{Ar}$), 122.79 (*C*H$_{imid}$), 122.72 (*C*H$_{imid}$), 54.89 (Ar*C*H$_2$N), 51.68 (Br*C*H$_2$CH$_2$N), 50.20 (BrCH$_2$*C*H$_2$N), 34.34 (*C*(CH$_3$)$_3$), 30.99 (C(*C*H$_3$)$_3$). ESI-MS (*m/z*): Calc. for $C_{16}H_{22}Br_2N_2$ [M−Br]$^+$: 321. Found: 321.

4.4. Synthesis of 1-benzyl-1′-methyl-3,3′-ethylenediimidazolium dibromide (**3a**)

A Schlenk flask was charged with a mixture of **2a** (1.0 g, 3.70 mmol), *N*-benzylimidazole (0.586 g, 3.70 mmol) and toluene (20 mL) and was stirred at 80 °C for 3 d under dinitrogen. A white precipitate was isolated, washed with THF (3 × 15 mL) and dried under vacuum to yield **3a** as a white powder. (1.43 g, 90%). ^{1}H NMR (DMSO-d_6): δ 9.32 (s, 1H, NC*H*N), 9.17 (s, 1H, NC*H*N), 7.86 (s, 1H, CH_{imid}), 7.77 (s, 1H, CH_{imid}), 7.72 (s, 1H, CH_{imid}), 7.64 (s, 1H, CH_{imid}), 7.48–7.36 (m, 5H, CH_{Ar}), 5.45 (s, 2H, ArCH_2N), 4.74 (s, 4H, NCH_2CH_2N), 3.84 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 137.11 (NCHN), 136.72 (NCHN), 134.57 ($C_{Ar(ipso)}$), 128.94 (*C*H$_{Ar}$), 128.73 (*C*H$_{Ar}$), 128.27 (*C*H$_{Ar}$), 123.82 (*C*H$_{imid}$), 122.88 (2C, *C*H$_{imid}$), 122.27 (*C*H$_{imid}$), 51.98 (Ar*C*H$_2$N), 48.55 (NCH$_2$CH$_2$N), 48.19 (NCH$_2$*C*H$_2$N), 35.98 (*C*H$_3$). ESI-MS (*m/z*): Calc. for $C_{16}H_{20}Br_2N_4$ [M−Br]$^+$: 347. Found: 347.

4.5. Synthesis of 1-(4-tert-butylbenzyl)-1′-methyl-3,3′-ethylenediimidazolium dibromide (**3b**)

A Schlenk flask was charged with a mixture of **2b** (0.85 g, 2.11 mmol), *N*-methylimidazole (0.179 mL, 2.26 mmol) and toluene (20 mL) and was stirred at 150 °C for 3 d under nitrogen atmosphere. A white precipitate was isolated, washed with toluene (3 × 15 mL) and dried under vacuum to yield **3b** as a white powder. (0.96 g, 94%). ^{1}H NMR (DMSO-d_6): δ 9.25 (s, 1H, NC*H*N), 9.12 (s, 1H, NC*H*N), 7.85 (s, 1H, CH_{imid}), 7.73 (s, 2H, CH_{imid}), 7.63 (s, 1H, CH_{imid}), 7.45 (d, J = 8.2, 2H, CH_{Ar}), 7.32 (d, J = 8.2, 2H, CH_{Ar}), 5.38 (s, 2H, ArCH_2N), 4.71 (s, 4H, NCH_2CH_2N), 3.84 (s, 3H, CH_3), 1.27 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 151.32 ($C_{Ar(para)}$), 137.11 (NCHN), 136.63 (NCHN), 131.66 ($C_{Ar(ipso)}$), 128.10 (*C*H$_{Ar}$), 125.74 (*C*H$_{Ar}$), 123.89 (*C*H$_{imid}$), 122.93 (*C*H$_{imid}$), 122.87 (*C*H$_{imid}$), 122.32 (*C*H$_{imid}$), 51.73 (Ar*C*H$_2$N), 48.60 (NCH_2CH$_2$N), 48.24 (NCH$_2$*C*H$_2$N), 35.99 (*C*H$_3$), 34.37 (*C*(CH$_3$)$_3$), 31.02 (C(*C*H$_3$)$_3$). ESI-MS (*m/z*): Calc. for $C_{20}H_{28}Br_2N_4$ [M−Br]$^+$: 403. Found: 403.

4.6. Synthesis of dibromo(1-benzyl-1′-methyl-3,3′-ethylenediimidazolin-2,2′-diylidene)disilver(I) (**4a**)

A suspension of **3a** (1.0 g, 2.34 mmol) and one equiv of Ag_2O (0.541 g, 2.34 mmol) in dichloromethane (25 mL) was stirred at room temperature for 2 h under dinitrogen in the absence of light. The color of the suspension gradually changed from black to white. The precipitate was then isolated, washed with dichloromethane (3 × 10 mL) and dried under vacuum to yield **4a** as a white powder (1.42 g, 95%). ^{1}H NMR (DMSO-d_6): δ 7.49 (s, 1H, CH_{imid}), 7.45 (s, 1H, CH_{imid}), 7.35 (t, J = 7.3, 2H, C$H_{Ar(meta)}$), 7.29 (t, J = 7.3, 1H, C$H_{Ar(para)}$), 7.27 (s, 1H, CH_{imid}), 7.16 (s, 1H, CH_{imid}), 7.09 (d, J = 7.3, 2H, C$H_{Ar(ortho)}$), 5.25 (s, 2H, ArCH_2N), 4.67-4.61 (m, 2H, NCH_2CH$_2$N), 4.58–4.51 (m, 2H, NCH$_2$CH_2N), 3.56 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 180.50 (NCN), 179.78 (NCN), 137.32 ($C_{Ar(ipso)}$), 128.67 (*C*H$_{Ar}$), 127.81 (CH$_{Ar(para)}$), 127.12 (*C*H$_{Ar}$), 122.88 (*C*H$_{imid}$), 122.74 (*C*H$_{imid}$), 122.57 (*C*H$_{imid}$), 121.93 (*C*H$_{imid}$), 53.93 (Ar*C*H$_2$N), 51.47 (NCH_2CH$_2$N), 50.64 (NCH$_2$*C*H$_2$N), 38.25 (*C*H$_3$). Anal. Calc. for $C_{16}H_{18}Br_2N_4Ag_2$: C, 29.94; H, 2.83; N, 8.73. Found: C, 29.78; H, 2.53; N, 8.59%.

4.7. Synthesis of dibromo[1-(4-tert-butylbenzyl)-1′-methyl-3,3′-ethylenediimidazolin-2,2′-diylidene]disilver(I) (**4b**)

A suspension of **3b** (0.403 g, 0.832 mmol) and one equiv of Ag_2O (0.193 g, 0.832 mmol) in dichloromethane (15 mL) was stirred at room temperature for 4 h under dinitrogen in the absence of light. The color of the suspension gradually changed from black to white. The precipitate was isolated, washed with dichloromethane (3 × 10 mL) and dried under vacuum to yield **4b** as a white powder (0.41 g, 70%). ^{1}H NMR (DMSO-d_6): δ 7.50 (s, 1H, CH_{imid}), 7.47 (s, 1H, CH_{imid}), 7.34 (d, J = 8.1, 2H, CH_{Ar}), 7.32 (s, 1H, CH_{imid}), 7.16 (s, 1H, CH_{imid}), 6.96 (d, J = 7.4, 2H, CH_{Ar}), 5.21 (s, 2H, ArCH_2N), 4.71–4.61 (m, 2H, NCH_2CH$_2$N), 4.58–4.50 (m, 2H, NCH$_2$CH_2N), 3.44 (s, 3H, CH_3), 1.23 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 180.58 (NCN), 179.83 (NCN), 150.22 ($C_{Ar(para)}$), 134.44 ($C_{Ar(ipso)}$), 126.75 (*C*H$_{Ar}$), 125.36 (*C*H$_{Ar}$), 122.98 (*C*H$_{imid}$), 122.65 (2C, *C*H$_{imid}$), 121.69 (*C*H$_{imid}$), 53.55 (Ar*C*H$_2$N), 51.50 (NCH_2CH$_2$N), 50.50 (NCH$_2$*C*H$_2$N), 38.14 (*C*H$_3$), 34.22 (*C*(CH$_3$)$_3$), 31.04 (C(*C*H$_3$)$_3$). Anal. Calc. for $C_{20}H_{26}Br_2N_4Ag_2$: C, 34.41; H, 3.75; N, 8.03. Found: C, 34.51; H, 3.42; N, 7.84%.

4.8. Synthesis of dichloro(1-benzyl-1′-methyl-3,3′-ethylenediimidazolin-2,2′-diylidene)palladium(II) (**5a**)

A suspension of **4a** (0.4 g, 0.62 mmol) and $PdCl_2$ (110 mg, 0.62 mmol) in DMF (10 mL) was stirred at 90 °C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5a** as a white powder. Crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a concentrated solution of the sample in DMF (0.14 g, 52%). ^{1}H NMR (DMSO-d_6): δ 7.45 (br s, 2H, CH_{imid}), 7.36 (br s, 1H, CH_{imid}), 7.32 (br s, 3H, C$H_{Ar(meta\ and\ para)}$), 7.26 (br s, 1H, CH_{imid}), 7.10 (br s, 2H, C$H_{Ar(ortho)}$), 6.08 (m, 1H, ArCH_aH$_b$N)), 5.41–5.22 (m, 2H, NCH_2CH$_2$N), 5.16 (m, 1H, ArCH$_a$$H_b$N), 4.69–4.40 (m, 2H, NCH$_2$CH_2N), 3.37 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 156.68 (NCN), 154.87 (NCN), 137.52 ($C_{Ar(ipso)}$), 128.62 (CH$_{Ar}$), 127.67 (CH$_{Ar(para)}$), 127.06 (CH$_{Ar}$), 123.49 (CH$_{imid}$), 123.27 (CH$_{imid}$), 122.79 (CH$_{imid}$), 122.64 (CH$_{imid}$), 52.71 (ArCH$_2$N), 46.94 (NCH$_2$CH$_2$N), 46.94 (NCH$_2$CH$_2$N), 37.26 (CH$_3$). ESI-MS (*m/z*): Calc. for $C_{16}H_{18}Cl_2N_4Pd_2$ [M−Cl]$^+$: 407. Found: 407.

4.9. Synthesis of dichloro[1-(4-tert-butylbenzyl)-1′-methyl-3,3′-ethylenediimidazolin-2,2′-diylidene]palladium(II) (**5b**)

A suspension of **4b** (0.203 g, 0.291 mmol) and $PdCl_2$ (50 mg, 0.282 mmol) in DMF (10 mL) was stirred at 90 °C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr formed. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5b** as a white powder. Crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a concentrated solution of the sample in DMF (84 mg, 60%). ^{1}H NMR (DMSO-d_6): δ 7.52–7.40 (br s, 2H, CH_{Ar}), 7.39–7.30 (br s, 3H, CH_{imid}), 7.26 (br s, 1H, CH_{imid}), 7.13–6.98 (br s, 2H, CH_{Ar}), 6.18–5.90 (m, 1H, ArCH_aH$_b$N), 5.32–5.11 (m, 3H, ArCH$_a$$H_b$N and NC$H_2CH_2$N), 4.68–4.35 (m, 2H, NCH$_2$CH_2N), 2.50 (s, 3H, CH_3), 1.27 (s, 9H, C(CH$_3$)$_3$). ^{13}C NMR (DMSO-d_6): δ 155.05 (NCN), 154.02 (NCN), 150.12 ($C_{Ar(para)}$), 134.59 ($C_{Ar(ipso)}$), 126.91 (CH$_{Ar}$), 125.34 (CH$_{Ar}$), 123.46 (CH$_{imid}$), 123.32 (CH$_{imid}$), 122.65 (CH$_{imid}$), 122.50 (CH$_{imid}$), 52.43 (ArCH$_2$N), 47.01 (NCH$_2$CH$_2$N), 46.87 (NCH$_2$CH$_2$N), 37.15 (CH$_3$), 34.23 (C(CH$_3$)$_3$), 31.07 (C(CH_3)$_3$). ESI-MS (*m/z*): Calc. for $C_{20}H_{26}Cl_2N_4Pd_2$ [M−Cl]$^+$: 463. Found: 463.

4.10. General procedure for the Suzuki coupling reactions

In a typical run, an oven dried 25 mL sealed tube equipped with a stir bar was charged with a known mol% catalyst, base (2.0 mmol) and phenylboronic acid (1.5 mmol). Under dinitrogen, dioxane (5 mL) and aryl halides (1.0 mmol) were added via syringe. The flask was placed in pre-heated sand bath at 80 °C. After the specified time the flask was removed from the sand bath and water (20 mL) was added followed by extraction with dichloromethane (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), dried over anhydrous $MgSO_4$, filtered and the internal standard (24 mg of dodecahydrotriphenylene) was added. Solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. Yields were determined by ^{1}H NMR against the internal standard dodecahydrotriphenylene.

4.11. X-ray structure determinations

Data was collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program [11]. Cell refinement and data reductions used the programs DENZO and SCALEPACK [12]. SIR97 [13] was used to solve the structures and SHELXL97 [14] was used to refine the structures. ORTEP-3 for Windows [15] was used for molecular graphics and PLATON [16] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

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Appendix A. Supplementary material

CCDC 690083, 687292 and 687293 contain the supplementary crystallographic data for **3a**, **5a** and **5b**·**DMF**. The 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.040.

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