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Synthesis, X-ray structures, and catalytic activities of (κ^2-*C,N*)-palladacycles bearing imidazol-2-ylidenes

M. Emin Günay [a,*], Rukiye Gümüşada [a], Namık Özdemir [b], Muharrem Dinçer [b], Bekir Çetinkaya [c]

[a] Department of Chemistry, Adnan Menderes University, 09010 Aydın, Turkey
[b] Department of Physics, Ondokuz Mayıs University, 55139, Kurupelit-Samsun, Turkey
[c] Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey

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ABSTRACT

Quaternisation of methylimidazole (**1**) by methyl substituted benzyl bromides afforded imidazolium salts (**2**) which were converted to (κ^2-*C,N*)-palladacycles bearing imidazol-2-ylidenes **6** or **7**, by either *in situ* deprotonation or *via* Ag–NHC intermediate (**3**), using the bridged palladacycles **4** or **5**, respectively. The palladacycles **6** and **7** were characterized by elemental analysis; NMR spectroscopy and the molecular structure of **6c** and **7c** were determined by X-ray crystallography. The complexes **6** and **7** display high activity in Suzuki–Miyaura coupling of a range of aryl bromides.

1. Introduction

Cyclopalladacycles received much attention for more than 40 years in coordination- and organometallic chemistry due to their specific structure, stability, and their role in various catalytic reactions [1–3]. Significant efforts have been devoted in derivatizing the basic skeletons in order to improve and tune their catalytic properties. Their electronic and steric properties are influenced by various factors, such as the size of the metallocyclic ring, the type of the donor atoms, and the nature of the co-ligands. In this context, palladacyclic complexes, derived from organic molecules bearing N-donor groups, have played a significant role that can operate at very low metal loadings [4]. Apparently palladacyclic catalysts alone are helpless and the modulation of activity of Pd catalyst by the co-ligands is required, e.g. in the case of unactivated aryl chlorides, as well as the reactions of aryl bromides at lower temperatures [5–10]. An interesting approach is to combine palladacycles as convenient Pd sources and special ligands in catalytic system, e.g. NHC ligands, and to use preformed 1:1 complex. These complexes are air stable, and thus are more convenient in handling than toxic phosphines derivatives [5].

NHC's have attracted our attention because a variety of *N*-benzyl-substituted NHC-based metal complexes have been found to exhibit high efficiency in various C–C bond forming reactions catalyzed by palladium [11–15]. Also, these ligand precursors can be easily synthesized from commercially available heterocycles. In contrast to the numerous known coordination complexes of *N*-benzyl substituted NHC's, the number of their cyclopalladated derivatives remain limited [16,17]. Therefore, the main aim of this study is to investigate the effect of sp^2 vs. sp^3 hybridized N's of the 5-membered palladacyclic ring.

2. Results and discussion

2.1. Preparation of ligands

The general route to the target NHC ligand precursors and palladacyclic complexes is shown in Scheme 1. Unsymmetrical imidazolium salts **2a–c** were synthesized by the reaction of **1** with 2,4,6-trimethylbenzyl, 2,3,5,6-tetramethylbenzyl or 2,3,4,5,6-pentamethylbenzyl bromides. The salts **2a–c** could be purified by recrystallization from ethanol and by addition of diethyl ether. The NMR spectroscopic data of **2a–c** agree with the proposed structures. In the ^{1}H NMR spectra of **2a–c**, the imidazolium protons appear at δ 10.16, 10.02, and 9.94 ppm, respectively. The ^{13}C NMR shift of the NCN sp^2 carbon atoms in **2a–c** appear between δ 140.1 and 137.5 ppm, respectively. Signals at δ 48.1–49.3 ppm correspond to the benzylic methylene carbon resonances for **2a–c**.

2.2. Synthesis of silver(I)–NHC and palladacyclic complexes

We prepared mononuclear palladacyclic NHC complexes from salts **2** by *in situ* deprotonation or *via* AgNHC complexes (**3**). Reac-

* Corresponding author. Tel.: +90 256 212 8498; fax: +90 256 213 5379.
E-mail address: megunay@adu.edu.tr (M. Emin Günay).

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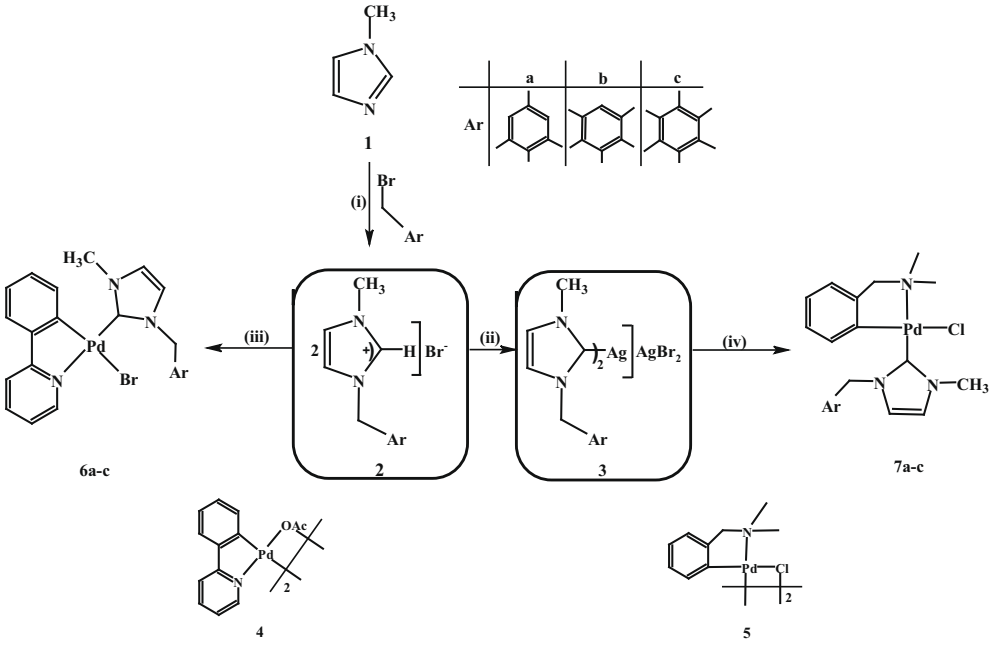


Scheme 1. *Reagents and conditions*: (i) PhMe, 25 °C; (ii) Ag_2O, CH_2Cl_2, 25 °C; (iii) **4**, PhMe, 110 °C; (iv) **5**, CH_2Cl_2, 25 °C.

tions of the imidazolium precursors with palladium dimer [Pd-(μ-OAc)(ppy)]$_2$ (ppy: 2-phenylpyridine), (**4**) in toluene at 110 °C gave the palladacyclic complexes **6a–c** in moderate yields. On the other hand, Pd analogs **7a–c** were synthesized by a transmetallation reaction between [Pd(dmba)(μ-Cl)]$_2$ (dmba: dimethylbenzylamine), (**5**) and the Ag-containing carbenes **3a–c** (Scheme 1) in CH_2Cl_2 at 25 °C. Since silver(I)–NHC complexes are easy to make and can be used as air-moisture-stable carbene transfer agent [18–23].

Solutions of complexes **6a–c** and **7a–c** in chlorinated solvents were observed to be stable toward air and moisture. The identities of the compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. All of the palladacyclic complexes exhibit characteristic ^{13}C chemical shifts which provide a useful diagnostic tool for metal carbene complexes. The chemical shifts for the carbene carbon atom (**6**, **7**) fall in the range δ 171.8–173.5 ppm.

In the ^{13}C NMR spectra of **7**, the chemical shifts of the carbene carbon atoms of the Pd–NHC complexes appear at $\delta \approx 182$ ppm, which is consistent with the chemical shifts of known Pd–NHC complexes [24].

2.3. Structural description of *6c* and *7c*

The structure of the complex **6c** is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The title complex contains a phenylpyridine (ppy) ligand, with a Pd^{II} metal centre, a 1-methyl-3-(2,3,4,5,6-pentamethylbenzyl)-2,3-dihydro-1H-imidazole ligand, and one bromine ligand. The coordination around the Pd^{II} ion is distorted *cis*-square-planar, and the Pd^{II} ion is coordinated by one pyridine N atom and one aryl C atom from the bidentate ligand, one carbenic C atom from the monodentate ligand, and one Br atom.

The two Pd–C bond distances are almost equal in magnitude [Pd1–C12 = 1.971(3) Å and Pd1–C11 = 1.980(3) Å] and the Pd1–C12 bond distance is comparable to those in other palladium(II)–NHC complexes [25–27]. The plane of the carbene ring is approximately orthogonal to the square plane [84.32(9)°] The bonding within the N-heterocyclic carbene (NHC) ring indicates a pattern

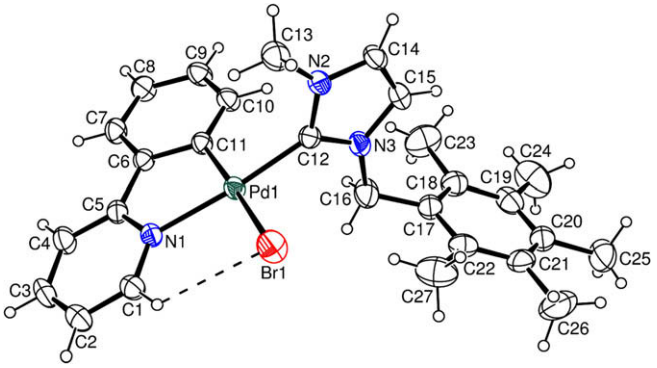


Fig. 1. A view of the complex (**6c**), showing 40% probability displacement ellipsoids and the atom-numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) for **6c**.

Bond lengths (Å)			
Pd1–C12	1.971 (3)	N2–C14	1.370 (4)
Pd1–C11	1.980 (3)	N2–C13	1.453 (4)
Pd1–N1	2.084 (2)	N3–C12	1.345 (4)
Pd1–Br1	2.5108 (4)	N3–C15	1.384 (4)
N1–C1	1.336 (4)	N3–C16	1.479 (4)
N2–C5	1.347 (4)	C14–C15	1.334 (4)
N2–C12	1.352 (3)	C16–C17	1.512 (5)
Bond angles (°)			
C12–Pd1–C11	91.15 (10)	C12–N3–C15	110.6 (2)
C12–Pd1–N1	172.46 (10)	C12–N3–C16	123.5 (2)
C11–Pd1–N1	81.30 (10)	C15–N3–C16	125.8 (3)
C12–Pd1–Br1	90.84 (7)	N3–C12–N2	104.9 (2)
C11–Pd1–Br1	175.27 (8)	N3–C12–Pd1	129.6 (2)
N1–Pd1–Br1	96.68 (6)	N2–C12–Pd1	125.5 (2)
C12–N2–C14	110.5 (2)	C15–C14–N2	107.4 (2)
C12–N2–C13	123.9 (2)	C15–C14–N3	106.5 (3)
C14–N2–C13	125.5 (2)	N3–C16–C17	112.5 (3)

of delocalization that extends from atom N2 to atom N3 through atom C12, the N2–C12 [1.352(3) Å] and N3–C12 [1.345(4) Å] distances being significantly shorter than the N2–C14 [1.370(4) Å]

and N3–C15 [1.384(4) Å] distances as is in similar NHC transition metal complexes [28–30].

The structure of the complex **7c** is shown in Fig. 2 and selected geometric parameters are listed in Table 2. The complex contains a *N*,*N*-dimethyl-1-phenylmethanamine ligand, with a Pd^{II} metal centre, a 1-methyl-3-(2,3,4,5,6-pentamethyl-benzyl)-2,3-dihydro-1H-imidazol-2-ylidene ligand, and one chlorine ligand. The coordination around the Pd^{II} ion is distorted *cis*-square-planar, and the Pd^{II} ion is coordinated by one amine N atom and one aryl C atom from the bidentate ligand, one carbenic C atom from the monodentate ligand, and one Cl atom.

The plane of the carbene ring is approximately orthogonal to the square plane 73.12(10), while the plane of the C17–C22 benzene ring is almost coplanar with the square plane 13.57(13). Similarly to the complex **6c**, the bonding within the N-heterocyclic carbene (NHC) ring indicates a pattern of delocalization that extends from atom N1 to atom N2 through atom C1, the N1–C1 [1.348(4) Å] and N2–C1 [1.350(4) Å] distances being significantly shorter than the N1–C2 [1.383(4) Å] and N2–C3 [1.387(4) Å] distances. These observations in complex **6c** and **7c** are possibly indicative of a greater partial double-bond character due to partial electron donation by nitrogen to the carbene C-atom donor [31,32]. Theoretical studies also indicate that the stability of these carbenes is due to electron donation from the N-atom lone pairs into the formally empty p(π) orbital on the carbene C atom (herein C1 and C12) [33,34].

The two coordinated C atoms in both complexes are *cis* to each other, which is in agreement with the fact that the donor groups with the largest *trans* influence avoid being mutually trans to one another. The change in geometrical parameters due to the difference of the bidentate ligand, does seem to significantly affect the coordination to the palladium(II) centre (Tables 1 and 2). Although the two Pd–C distances in both complex are in same magnitude, the Pd–N bond distances are significantly different. The Pd–N bond in complex **6c** is shorter than that in complex **7c**. It can be inferred from this result that the trans influence of carbene C atom in complex **7c** is larger than that in complex **6c**. However, the bite angle is not affected by the difference of the bidentate ligand and remains nearly constant. The difference between the Pd–N bond distances in both complexes can also be attributed to the different hybridization of the N*sp*2 and N*sp*3 atoms. The single-crystal data and X-ray collection parameters are given in Table 3.

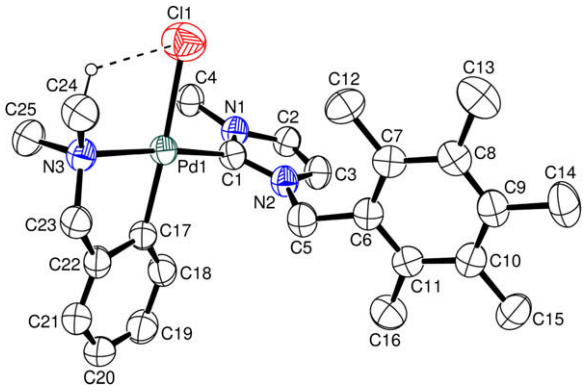


Fig. 2. A view of the complex (**7c**), showing 40% probability displacement ellipsoids and the atom-numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) for **7c**.

Bond Lengths [Å]			
Pd1–C1	1.973 (3)	N2–C3	1.387 (4)
Pd1–C17	1.973 (3)	N2–C5	1.477 (4)
Pd1–N3	2.147 (2)	N3–C25	1.466 (4)
Pd1–Cl1	2.4360 (8)	N3–C23	1.488 (4)
N1–C1	1.348 (4)	N3–C24	1.467 (4)
N1–C2	1.383 (4)	C2-C3	1.331 (5)
N1–C4	1.449 (4)	C5-C6	1.507 (4)
N2–C1	1.350 (4)	C22-C23	1.487 (5)
Bond Angles [deg]			
C1–Pd1–C17	91.86 (12)	C1–N1–C2	110.8 (3)
C1–Pd1–N3	174.40 (10)	C1–N1–C4	124.3 (3)
C17–Pd1–N3	82.54 (11)	C2–N1–C4	124.9 (3)
C1–Pd1–Cl1	91.31 (9)	C1–N2–C3	110.2 (2)
C17–Pd1–Cl1	176.56 (9)	C1–N2–C5	123.7 (3)
N3–Pd1–Cl1	94.28 (7)	C3–N2–C5	126.0 (3)
C25–N3–C23	109.6 (3)	N2–C1–N1	105.0 (2)
C25–N3–C24	109.0 (3)	N2–C1–Pd1	127.7 (2)
C23–N3–C24	109.5 (3)	N1–C1–Pd1	127.4 (2)
C25–N3–Pd1	107.8 (2)	C3–C2–N1	106.7 (3)
C23–N3–Pd1	105.07 (18)	C2–C3–N2	107.3 (3)
C24–N3–Pd1	115.8 (2)	N2–C5–C6	114.0 (3)

2.4. Catalytic studies

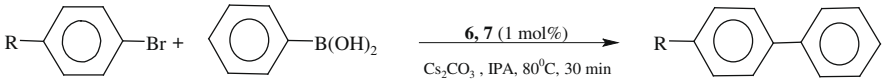
Since its discovery in 1979 [35], the Suzuki–Miyaura reaction is one of the most important transformations leading to the construction of unsymmetrical biphenyls. Pioneering work in the use of palladacycles for the Suzuki–Miyaura reaction was performed by Herrmann and co-workers using a phosphine-bearing palladacycle in the coupling reaction [36]. Good activity is not limited to phosphines donor systems because N-donor palladacycles have also been described with good results [37,38]. A preliminary Suzuki reaction was then conducted in the presence of palladacyclic complexes **6** and **7**. The coupling of aryl bromides with phenylboronic acid in 2-propanol with 1 mol% catalyst loading, and a reaction

Table 3
Summary of X-ray crystallographic data for complex **6c** and **7c**.

Parameter	**6c**	**7c**
Empirical formula	$C_{27}H_{30}BrN_3Pd$	$C_{25}H_{34}ClN_3Pd$
Crystal size (mm)	0.47 × 0.42 × 0.38	0.65 × 0.37 × 0.09
M_r	582.85	518.43
T (K)	296	296
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	27.5032 (9)	9.1975 (3)
b (Å)	9.1670 (3)	10.1400 (4)
c (Å)	19.6139 (7)	12.8922 (5)
α (°)	90	90.728 (3)
β (°)	96.876 (3)	91.709 (4)
γ (°)	90	91.728 (3)
V (Å^3)	4909.5 (3)	1201.17 (8)
Z	8	2
ρ_{calcd} (Mg/m^3)	1.577	1.433
μ (mm^{-1})	2.40	0.90
θ Range (°)	1.49–26.78	1.58–27.57
İndex ranges	$-34 \leqslant h \leqslant 34$, $-11 \leqslant k \leqslant 11$, $-24 \leqslant l \leqslant 24$	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 16$
Number of observed reflections	17 280	28321
Number of independent reflections	5222	5532
Number of parameters	289	280
Goodness-of-fit (GOF) on F^2	1.040	1.059
max/min $\Delta\rho$ (e Å^{-3})	0.45, −0.64	0.08, −0.02
R, wR (observed data)[a]	0.0323, 0.0749	0.0356, 0.1035
R, wR (all data)[a]	0.0418, 0.0781	0.0402, 0.1064

[a] Refinement method, full-matrix least squares on F^2.

Table 4
Suzuki–Miyaura cross-coupling reactions with aryl halides. Optimization of reaction parameter.[a]



Entry	Pd–NHC	R	Yield (%) [b,c]
1	**6a**	H	96
2	**6a**	Me	81
3	**6a**	$CH_3(O)C$	88
4	**6b**	H	99
5	**6b**	Me	84
6	**6b**	$CH_3(O)C$	91
7	**6c**	H	99
8	**6c**	Me	83
9	**6c**	$CH_3(O)C$	92
10	**7a**	H	50
11	**7a**	Me	68
12	**7a**	$CH_3(O)C$	89
13	**7b**	H	99
14	**7b**	Me	62
15	**7b**	$CH_3(O)C$	94
16	**7c**	H	85
17	**7c**	Me	67
18	**7c**	$CH_3(O)C$	93

[a] *Reagents*: an aryl halide (0.50 mmol), $PhB(OH)_2$ (0.75 mmol), Cs_2CO_3 (1.50 mmol), diethyleneglicol di-*n*-butyl ether (0.3 mmol, internal standard), palladacyclic catalyst (1 mol%), and 2-propanol (3 mL).
[b] Yields based on the aryl halide and average of two runs.
[c] All reactions were monitored by GC.

time of 30 min was chosen as a standard test reaction. The couplings occurred readily with **6a–c** and **7a–c** using Cs_2CO_3 as a base. The results summarized in Table 4 indicate that NHC-bearing palladacyclic complexes exhibit excellent activity at low catalyst loadings when aryl bromides, both activated and unactivated are used as substrates. Generally **6** are more effective than **7**. This difference may be due to stability of palladacycle in complex **6** relative to **7**. Alteration of the benzyl substituent of the NHC ligand has not shown a strong influence on the catalytic performance of the derived catalyst. However, as the number of methyl group increases on the benzyl substituent, the efficiency slightly increases.

Aryl bromide substrates have shown different reactivities under similar conditions. For example, complex **6** was found to be highly active in the C–C coupling of phenyl bromide and phenylboronic acid, giving almost quantitative conversions (entries 1, 4 and 7). In contrast to the literature reports and expectations, the reaction of activated substrate, *p*-bromoacetophenone, was slightly more difficult (entries 3, 6 and 9). The reason for this difference is not clear at this stage.

3. Conclusion

Facile synthesis and characterization of six new NHC complexes incorporating (κ^2-*C,N*)-palladacyclic frame (**6a–c** and **7a–c)** have been reported. The identity of **6c** and **7c** has been confirmed by X-ray diffraction studies and C_{carb} is found to be in *trans* configuration to N atom. Preliminary catalytic study revealed that the new complexes are active in the Suzuki–Miyaura cross-coupling reactions with aryl bromides. It is of interest that the 2-phenylpyridine derived palladacycle (**6**) exhibited higher catalytic activity than the *N,N*-dimethylbenzylamine derived palladacycle (**7**) under the same conditions. This difference may be due to the stability of 5-membered ring of the palladacycle in **6**. The efficiency also slightly depends on the NHC ligand and increases as the number of Me groups on the benzyl substituent increases on N^3 atom.

4. Experimental

4.1. General procedures

All reactions for the preparations of **6a–c** and **7a–c** were carried out under argon in flame-dried glassware using standard Schlenk-type flask. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. 1-Methylimidazole (**1**) was purchased from Merck. Palladium dimers **4** and **5** were also prepared according to the literature, respectively [39,40]. ^1H and ^{13}C NMR measurements were performed using a Varian Mercury AS 400 spectrometer operating at 400 and 100 MHz, respectively. Catalytic studies were analyzed using a gas chromatograph (HP, Agilant-6890N). Chemical shifts (δ) are relative to TMS. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

4.2. General procedure for the preparation of *2*

The benzyl bromide derivative [41] (20 mmol) and 1-methylimidazole (1.6 mL, 20 mmol) were stirred in toluene (15 mL) for 3 h at room temperature. The volume of the solution was reduced to 5 mL, diethyl ether was added to the remaining solution, which was vigorously shaken and then decantated. The solid residue was washed with diethyl ether (3 × 20 mL) to obtain a white solid, which was recrystallized from ethanol/diethyl ether (3 mL/15 mL).

4.2.1. Compound *2a*

Yield: 5.37 g, 91%, m.p.: 117–118 °C. ^1H NMR (δ, $CDCl_3$): 2.26 [s, 6H, $C_6H_2(CH_3)_3$]; 2.38 [s, 3H, $C_6H_2(CH_3)_3$]; 4.10 [s, 3H, NCH_3]; 5.53 [s, 2H, $NCH_2C_6H_2(CH_3)_3$]; 6.87 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 6.90 [s, 2H, $C_6H_2(CH_3)_3$]; 7.46 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 10.16 [s, 1H, NCHN]. ^{13}C NMR (δ, $CDCl_3$): 20.0 [$C_6H_2(CH_3)_3$]; 21.2 [$C_6H_2(CH_3)_3$]; 37.2 [NCH_3]; 48.1 [$NCH_2C_6H_2(CH_3)_3$]; 120.9 [$NCHCHNCH_3$]; 124.0 [$NCHCHNCH_3$]; 125.5, 130.1, 137.0, 138.3 [$C_6H_2(CH_3)_3$]; 140.1 [NCHN].

*4.2.2. Compound **2b***

Yield: 5.13 g, 83%, m.p.: 123–125 °C. ^{1}H NMR (δ, $CDCl_3$): 2.16 [s, 6H, $C_6H(CH_3)_4$]; 2.21 [s, 6H, $C_6H(CH_3)_4$]; 4.09 [s, 3H, NCH_3]; 5.59 [s, 2H, $NCH_2C_6H(CH_3)_4$]; 6.90 [d, 1H, J = 1.6 Hz, NCHCHN]; 7.01 [s, 1H, $C_6H(CH_3)_4$]; 7.51 [d, 1H, J = 1.6 Hz, NCHCHN]; 10.02 [s, 1H, NCHN]. ^{13}C NMR (δ, $CDCl_3$): 16.1 [$C_6H(CH_3)_4$]; 20.6 [$C_6H(CH_3)_4$]; 37.3 [NCH_3]; 48.8 [$NCH_2C_6H(CH_3)_4$]; 121.1 [$NCHCHNCH_3$]; 123.8 [$NCHCHNCH_3$]; 128.1, 133.8, 134.3, 135.2 [$C_6H(CH_3)_4$]; 137.2 [NCHN].

*4.2.3. Compound **2c***

Yield: 6.08 g, 94%, m.p.: 192–194 °C. ^{1}H NMR (δ, $CDCl_3$): 2.17 [s, 6H, $C_6(CH_3)_5$]; 2.18 [s, 6H, $C_6(CH_3)_5$]; 2.21 [s, 3H, $C_6(CH_3)_5$]; 4.08 [s, 3H, NCH_3]; 5.57 [s, 2H, $NCH_2C_6(CH_3)_5$]; 6.91 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 7.54 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 9.94 [s, 1H, NCHN]. ^{13}C NMR (δ, $CDCl_3$): 17.0 [$C_6(CH_3)_5$]; 17.1 [$C_6(CH_3)_5$]; 17.4 [$C_6(CH_3)_5$]; 37.2 [NCH_3]; 49.3 [$NCH_2C_6(CH_3)_5$]; 121.1 [$NCHCHNCH_3$]; 123.9 [$NCHCHNCH_3$]; 125.4, 133.8, 133.9, 136.9 [$C_6(CH_3)_5$]; 137.5 [NCHN].

*4.3. Preparation of Ag–NHC complexes **3a–c***

A suspension of **2a–c** and an equivalent amount Ag_2O (0.063 g, 0.27 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 8 h. The colour of the suspension gradually changed from black to colorless. The suspension was then filtered, washed with CH_2Cl_2 and dried under vacuum to give a white solid. Purification was achieved by repeated recrystallization from CH_2Cl_2/ether.

*4.3.1. Compound **3a***

Yield: 0.243 g, 71%; m.p.: 162–163 °C. ^{1}H NMR (δ, $CDCl_3$): 2.25 [s, 12H, $C_6H_2(CH_3)_3$]; 2.29 [s, 6H, $C_6H_2(CH_3)_3$]; 3.86 [s, 6H, NCH_3]; 5.30 [s, 4H, $NCH_2C_6H_2(CH_3)_3$]; 6.55 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.91 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.92 [s, 4H, $C_6H_2(CH_3)_3$]. ^{13}C NMR (δ, $CDCl_3$): 20.2 [$C_6H_2(CH_3)_3$]; 21.2 [$C_6H_2(CH_3)_3$]; 39.3 [NCH_3]; 49.8 [$NCH_2C_6H_2(CH_3)_3$]; 120.1 [$NCHCHNCH_3$]; 121.9 [$NCHCHNCH_3$]; 127.8, 129.9, 138.0, 139.2 [Ar–*C*]; 182.3 [Ag–$C_{carbene}$].

*4.3.2. Compound **3b***

Yield: 0.222 g, 66%; m.p.: 157–158 °C. ^{1}H NMR (δ, $CDCl_3$): 2.17 [s, 12H, $C_6H(CH_3)_4$]; 2.25 [s, 12H, $C_6H(CH_3)_4$]; 3.86 [s, 6H, NCH_3]; 5.36 [s, 4H, $NCH_2C_6H(CH_3)_4$]; 6.57 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.90 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 7.04 [s, 2H, $C_6H(CH_3)_4$]. ^{13}C NMR (δ, $CDCl_3$): 16.1 [$C_6H(CH_3)_4$]; 20.7 [$C_6H(CH_3)_4$]; 39.3 [NCH_3]; 50.4 [$NCH_2C_6H(CH_3)_4$]; 120.4 [$NCHCHNCH_3$]; 121.8 [$NCHCHNCH_3$]; 130.6, 132.9, 134.0, 134.9 [Ar–*C*]; 182.2 [Ag–$C_{carbene}$].

*4.3.3. Compound **3c***

Yield: 0.238 g, 72%; m.p.: 148–149 °C. ^{1}H NMR (δ, $CDCl_3$): 2.21 [s, 12H, $C_6(CH_3)_5$]; 2.24 [s, 12H, $C_6(CH_3)_5$]; 2.27 [s, 6H, $C_6(CH_3)_5$]; 3.86 [s, 6H, NCH_3]; 5.36 [s, 4H, $NCH_2C_6(CH_3)_5$]; 6.59 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.90 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]. ^{13}C NMR (δ, $CDCl_3$): 17.0 [$C_6(CH_3)_5$]; 17.1 [$C_6(CH_3)_5$]; 17.4 [$C_6(CH_3)_5$]; 39.3 [NCH_3]; 50.8 [$NCH_2C_6(CH_3)_5$]; 120.5 [$NCHCHNCH_3$]; 121.8 [$NCHCHNCH_3$]; 127.8, 133.6, 133.7, 136.7 [Ar–*C*]; 181.9 [Ag–$C_{carbene}$].

*4.4. General procedure for the preparation of complexes **6** and **7***

*4.4.1. Preparation of complexes **6***

A sample of $[Pd(\mu\text{-}OAc)_2(ppy)]_2$ (0.150 g, 0.23 mmol) was refluxed with one of the compounds of type **2** (0.46 mmol) in toluene (10 mL) at 110 °C for 12 h. The solvent was removed *in vacuo*, the remaining precipitate was then dissolved in dichloromethane (2 mL) and recrystallization from dichloromethane/diethyl ether afforded the complexes of type **6** (2 mL/10 mL).

*4.4.2. Preparation of complexes **7***

A 50 mL Schlenk tube was charged with silver compound, **3** (0.46 mmol), $[Pd(dmba)(\mu\text{-}Cl)]_2$ (0.150 g, 0.27 mmol) and 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 24 h. The resulting solution was then filtered and recrystallized from dichloromethane/diethyl ether to give as a white solid.

*4.4.3. Compound **6a***

Yield: 0.072 g, 55%, m.p.: 196–198 °C. ^{1}H NMR (δ, $CDCl_3$): 2.24 [s, 6H, $C_6H_2(CH_3)_3$]; 2.28 [s, 3H, $C_6H_2(CH_3)_3$]; 3.98 [s, 3H, NCH_3]; 5.36 [d, 1H, J = 16 Hz, $NCHCHNCH_3$]; 5.69 [d, 1H, J = 16 Hz, $NCHCHNCH_3$]; 6.18 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 6.39 [s, 2H, $NCH_2C_6H_2(CH_3)_3$]; 6.89 [s, 2H, $C_6H_2(CH_3)_3$]; 6.94 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.10 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.22 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.59 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 7.73 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 7.81 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 9.54 [d, 1H, J = 8.0 Hz, pyridyl-CH]. ^{13}C NMR (δ, $CDCl_3$): 20.2 [$C_6H_2(CH_3)_3$]; 21.2 [$C_6H_2(CH_3)_3$]; 38.9 [NCH_3]; 49.7 [$NCH_2C_6H_2(CH_3)_3$]; 118.3 [$NCHCHNCH_3$)]; 119.5 [Ar-*C*]; 121.6 [$NCHCHNCH_3$)]; 122.6, 124.1, 124.4, 127.9, 129.5, 129.9, 136.4, 138.6, 138.7, 138.8, 146.9, 151.4, 155.7, 164.5 [Ar–*C*]; 173.5 [Pd–$C_{carbene}$]. Anal. Calc. for $C_{25}H_{26}BrN_3Pd$ (554.81): C, 54.12; H, 4.72; N, 7.57. Found: C, 54.43; H, 4.26; N, 7.98%.

*4.4.4. Compound **6b***

Yield: 0.075 g, 54%, m.p.: 180–182 °C. ^{1}H NMR (δ, $CDCl_3$): 2.16 [s, 6H, $C_6H(CH_3)_4$]; 2.22 [s, 6H, $C_6H(CH_3)_4$]; 3.98 [s, 3H, NCH_3]; 5.44 [d, 1H, J = 16 Hz, $NCHCHNCH_3$]; 5.75 [d, 1H, J = 12 Hz, $NCHCHNCH_3$]; 6.20 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 6.39 [s, 2H, $NCH_2C_6H(CH_3)_4$]; 6.88 [s, 1H, $C_6H(CH_3)_4$]; 6.97 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.10 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.22 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.59 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 7.74 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 7.81 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 9.55 [d, 1H, J = 8.0 Hz, pyridyl-CH]. ^{13}C NMR (δ, $CDCl_3$): 16.2 [$C_6H(CH_3)_4$]; 20.6 [$C_6H(CH_3)_4$]; 38.9 [NCH_3]; 50.5 [$NCH_2C_6H(CH_3)_4$]; 118.3 [$NCHCHNCH_3$]; 119.9 [Ar–*C*]; 121.5 [$NCHCHNCH_3$]; 122.6, 124.0, 124.4, 129.9, 130.8, 132.5, 134.5, 134.8, 136.5, 138.6, 146.9, 151.5, 155.8, 164.5 [Ar–*C*]; 173.4 [Pd–$C_{carbene}$]. Anal. Calc. for $C_{26}H_{28}BrN_3Pd$ (568.84): C, 54.90; H, 4.96; N, 7.39. Found: C, 54.75; H, 4.19; N, 7.28%.

*4.4.5. Compound **6c***

Yield: 0.128 g, 70%, m.p.: 279–280 °C. ^{1}H NMR (δ, $CDCl_3$): 2.20 [s, 12H, $C_6(CH_3)_5$]; 2.25 [s, 3H, $C_6(CH_3)_5$]; 3.98 [s, 3H, NCH_3]; 5.44 [d, 1H, J = 16 Hz, $NCHCHNCH_3$]; 5.75 [d, 1H, J = 12 Hz, $NCHCHNCH_3$]; 6.20 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 6.43 [s, 2H, $NCH_2C_6(CH_3)_5$]; 6.95 [t, 1H, J = 8.0 Hz; pyridyl-CH]; 7.10 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.22 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 7.59 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 7.73 [d, 1H, J = 8.0 Hz, pyridyl-CH]; 7.80 [t, 1H, J = 8.0 Hz, pyridyl-CH]; 9.55 [d, 1H, J = 8.0 Hz, pyridyl-CH]. ^{13}C NMR (δ, $CDCl_3$): 17.0 [$C_6(CH_3)_5$]; 17.2 [$C_6(CH_3)_5$]; 17.3 [$C_6(CH_3)_5$]; 38.9 [NCH_3]; 50.9 [$NCH_2C_6(CH_3)_5$]; 118.3 [$NCHCHNCH_3$]; 120.1 [Ar–*C*]; 121.4 [$NCHCHNCH_3$]; 122.6, 124.0, 124.4, 128.2, 129.9, 133.2, 134.4, 135.9, 136.5, 138.6, 146.9, 151.4, 155.8, 164.5 [Ar–*C*]; 173.2 [Pd–$C_{carbene}$]. Anal. Calc. for $C_{27}H_{30}BrN_3Pd$ (582.87): C, 55.64; H, 5.19; N, 7.21. Found: C, 55.70; H, 5.15; N, 7.10%.

*4.4.6. Compound **7a***

Yield: 0.158 g, 82%, m.p.: 204–205 °C. ^{1}H NMR (δ, $CDCl_3$): 2.23 [s, 6H, $C_6H_2(CH_3)_3$-*o*-CH_3]; 2.28 [s, 3H, C_6H_2 $(CH_3)_3$-*p*-CH_3]; 2.84 [s, 3H, $CH_2N(CH_3)_2$]; 2.85 [s, 3H, $CH_2N(CH_3)_2$]; 3.97 [s, 3H, NCH_3]; 5.38 [d, 1H, J = 12 Hz, $NCHCHNCH_3$]; 5.67 [d, 1H, J = 12 Hz,

NC*H*CHNCH$_3$]; 6.04 [d, 1H, J = 8 Hz, C$_6H_4$]; 6.38 [s, 2H, NCH_2C$_6$H$_2$(CH$_3$)$_3$]; 6.75 [t, 1H, J = 8 Hz, C$_6H_4$]; 6.83 [s, 2H, NCH_2C$_6H_4$]; 6.88 [s, 2H, C$_6H_2$(CH$_3$)$_3$]; 6.95 [t, 1H, J = 8 Hz, C$_6H_4$]; 7.02 [d, 1H, J = 8 Hz, C$_6H_4$]. ^{13}C NMR (δ, CDCl$_3$): 20.2 [C$_6$H$_2$(CH$_3$)$_3$-*o*-*C*H$_3$]; 21.2 [C$_6$H$_2$(CH$_3$)$_3$-*p*-*C*H$_3$]; 38.9 [N*C*H$_2$C$_6$H$_2$(CH$_3$)$_3$]; 49.7 [N*C*H$_3$]; 50.3 [CH$_2$N(*C*H$_3$)$_2$]; 50.5 [CH$_2$N(*C*H$_3$)$_2$]; 72.4 [*C*H$_2$N(CH$_3$)$_2$]; 119.5 [NCH*C*HNCH$_3$]; 121.5 [NCH*C*HNCH$_3$]; 122.5, 123.9, 125.7, 128.3, 129.5, 135.9, 138.6, 138.8, 148.8, 148.9 [Ar–*C*]; 173.1 [Pd–$C_{carbene}$]. Anal. Calc. for C$_{23}$H$_{30}$ClN$_3$Pd (490.37): C, 56.33; H, 6.17; N, 8.57. Found: C, 55.98; H, 5.95; N, 8.13%.

4.4.7. Compound **7b**

Yield: 0.178 g, 90%, m.p.: 205–206 °C. ^{1}H NMR (δ, 400 MHz, CDCl$_3$): 2.15 [s, 6H, C$_6$H(CH$_3$)$_4$-*o*-*C*H$_3$]; 2.22 [s, 6H, C$_6$H (CH$_3$)$_4$-*m*-*C*H$_3$]; 2.85 [s, 3H, CH$_2$N(*C*H$_3$)$_2$]; 2.86 [s, 3H, CH$_2$N(*C*H$_3$)$_2$]; 3.98 [s, 3H, N*C*H$_3$]; 5.46 [d, 1H, J = 16 Hz, NCH*C*HNCH$_3$]; 5.75 [d, 1H, J = 16 Hz, N*C*HCHNCH$_3$]; 6.06 [d, 1H, J = 8 Hz, C$_6H_2$], 6.37 [s, 2H, NCH_2C$_6$H(CH$_3$)$_4$]; 6.77 [t, 1H, J = 8 Hz, C$_6H_2$]; 6.81 [s, 2H, NCH_2C$_6H_4$]; 6.98 [t, 1H, J = 8 Hz, C$_6H_2$]; 6.99 [s, 1H, C$_6$*H*(CH$_3$)$_4$]; 7.03 [d, 1H, J = 8 Hz, C$_6H_2$]. ^{13}C NMR (δ, 100 MHz, CDCl$_3$): 14.9 [C$_6$H(CH$_3$)$_4$-*o*-*C*H$_3$]; 19.4 [C$_6$H(CH$_3$)$_4$-*m*-*C*H$_3$]; 37.7 [NCH$_2$C$_6$H(CH$_3$)$_4$]; 49.1 [N*C*H$_3$]; 49.2 [CH$_2$N(*C*H$_3$)$_2$]; 71.2 [*C*H$_2$N(CH$_3$)$_2$]; 118.5 [NCH*C*HNCH$_3$]; 120.1 [N*C*HCHNCH$_3$]; 121.3, 122.7, 124.5, 129.8, 131.2, 133.2, 133.6, 134.8, 147.6, 147.7 [Ar–*C*]; 171.8 [Pd–$C_{carbene}$]. Anal. Calc. for C$_{24}$H$_{32}$ClN$_3$Pd (504.40): C, 57.15; H, 6.39; N, 8.33. Found: C, 56.88; H, 6.11; N, 8.03%.

4.4.8. Compound **7c**

Yield: 0.172 g, 85%, m.p.: 225–226 °C. ^{1}H NMR (δ, 400 MHz, CDCl$_3$): 2.19 [s, 6H, C$_6$(CH$_3$)$_5$-*o*-*C*H$_3$]; 2.21 [s, 6H, C$_6$(CH$_3$)$_5$-*m*-*C*H$_3$]; 2.25 [s, 3H, C$_6$(CH$_3$)$_5$-*p*-*C*H$_3$]; 2.85 [s, 6H, CH$_2$N(*C*H$_3$)$_2$]; 3.97 [s, 3H, N*C*H$_3$]; 5.46 [d, 1H, J = 16 Hz, NCH*C*HNCH$_3$]; 5.76 [d, 1H, J = 16 Hz, N*C*HCHNCH$_3$]; 6.04 [d, 1H, J = 8 Hz, C$_6H_2$]; 6.40 [s, 2H, NCH_2C$_6$(CH$_3$)$_5$]; 6.77 [t, 1H, J = 8 Hz, C$_6H_2$]; 6.80, [s, 2H, NCH_2C$_6H_4$]; 6.96 [t, 1H, J = 8 Hz, C$_6H_2$], 7.03 [d, 1H, J = 8 Hz, C$_6H_2$]. ^{13}C NMR (δ, 100 MHz, CDCl$_3$): 17.0 [C$_6$(CH$_3$)$_5$-*o*-*C*H$_3$]; 17.2 [C$_6$(CH$_3$)$_5$-*m*-*C*H$_3$]; 17.3 [C$_6$(CH$_3$)$_5$-*p*-*C*H$_3$]; 38.9 [NCH$_2$C$_6$(CH$_3$)$_5$]; 50.4 [CH$_2$N(*C*H$_3$)$_2$]; 50.9 [N*C*H$_3$]; 72.4 [NC*H*$_2$C$_6H_4$]; 119.9 [NCH*C*HNCH$_3$]; 121.2 [N*C*HCHNCH$_3$]; 122.5, 123.9, 125.7, 128.4, 133.2, 134.3, 135.9, 140.0, 148.8, 148.9 [Ar–*C*]; 172.9 [Pd–$C_{carbene}$]. Anal. Calc. for C$_{25}$H$_{34}$ClN$_3$Pd (518.43): C, 57. 92; H, 6.61; N, 8.11. Found: C, 57.81; H, 6.45; N, 7.98%.

4.5. General procedure for the Suzuki coupling reactions

In a typical run, a two-necked 25 mL flask fitted with a reflux condenser and septum was charged with aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), Cs_2CO_3 (1.5 mmol), diethyleneglicol di-*n*-butyl ether (0.3 mmol, internal standard) and the palladacyclic catalyst (1 mol%) in 3 mL of 2-propanol were added. The flask was placed in a preheated oil bath (80 °C) under an argon atmosphere. At the completion of the reaction, the mixture was cooled, added 2-propanol, filtered through a pad of silica gel with copious washing, then concentrated and purified by flash chromatography on silica gel. The reactions were monitored by gas chromatography and the yields were based on aryl bromide.

4.6. X-ray crystal structure determination

Diffraction data for **6c** and **7c** were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at 296 K. The structures were solved by direct-methods using program SHELXS-97 [42]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods using program SHELXL-97 [43]. All hydrogen atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.97 and 0.93 Å for CH$_3$, CH$_2$ and aromatic CH, respectively. The displacement parameters of the H atoms were constrained as U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for methyl) of the carrier atom. Data collection: X-AREA [42]; cell refinement: X-AREA; data reduction: X-RED32 [44]; molecular graphics: ORTEP-3 *for Windows* [45]; software used to prepare material for publication: WINGX [46] and PLATON [47].

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Appendix A. Supplementary data

CCDC 699017 and 699018 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.034.

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