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The synthesis, characterization, and catalytic properties of $(\kappa^2 - C, N)$-palladacycles with N-heterocyclic carbene-based ancillary ligands

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Abstract: Novel five-membered (κ^2-C,N)-palladacyclic complexes were prepared from the reaction of the corresponding acetate-bridged palladacycle dimer with N-heterocyclic carbene (NHC) ligands in high yields. Palladacyclic complexes (**3**) were fully characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. Palladacyclic complexes were tested as catalyst for the C–C bond forming reaction. These complexes were found to be efficient catalysts for the Suzuki–Miyaura reaction of aryl bromides.

Key words: Palladacycle, N-heterocyclic carbene ligand, Suzuki–Miyaura reaction

1. Introduction

Palladacycles, in which the ligand is in a position to coordinate to the metal center through both a metalated carbon and a donor atom, are one of the most popular and studied classes of organopalladium derivatives.[1–3] In the last decade, palladacycles have also emerged as a very promising family of organometallic catalyst precursors in particular due to their facile synthesis, thermal stability, and possibility of modulating their steric and electronic properties.[4–8] The vast majority of these compounds possess anionic four-electron (C,Y-bidentate) or six-electron (YCY′ tridentate) donor ligands (YCY′ could be N, P, O, As, Se, or S). Depending on their electronic and steric properties, they may show different catalytic activity. Cyclopalladated compounds (also called palladacycles) are the most active catalysts for C-C and C–heteroatom bond-forming reactions among the catalysts reported.[5,9,10] The Suzuki-Miyaura reaction, which is the direct cross-coupling of an aryl halide with boron-containing reagents in the presence of palladium catalyst, is arguably one of the easiest and most widely applied cross-coupling methods.[11,12]

Furthermore, N-heterocyclic carbenes (NHCs) have attracted increasing interest as ancillary ligands, leading to many applications in the field of transition metal catalysis such as Pd-catalyzed cross-coupling reactions,[13] transfer hydrogenation,[14] olefin metathesis,[15] and hydrosilylation.[16] Actually, palladacyclic complexes have found applications in a broad range of C–C cross-coupling reactions, while palladacycles complexes bearing N-heterocyclic carbene ligands have received less attention.[17] Inspired by the fact that palladium complexes with sterically hindered imidazole ligands exhibited attractive catalytic activity in C–C cross-coupling reactions,[18–20] we decided to examine whether a sterically hindered imidazole-2-ylidene ligand can improve the reactivity of palladacycles. However, if palladacycle catalysts are inadequate alone, modifications of Pd

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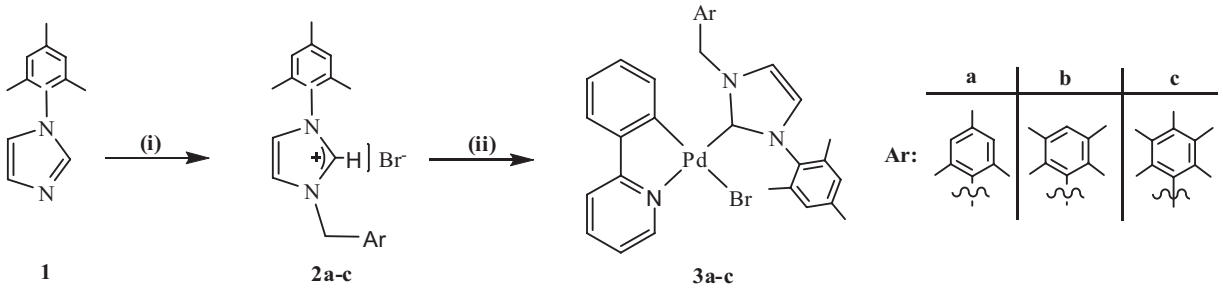
catalysts are required. In such cases, special ligands such as bulky and electron-rich phosphine are essential. To overcome this problem, we focused on the synthesis of hybrid palladacycles. Thus, we managed to combine palladacycles as convenient Pd sources and N-heterocyclic carbene ligands in the same structure.

Herein, we report studies of reactions of palladacycles with imidazol-2-ylidene resulting in the formation of monomeric five-membered $(\kappa^2 - C, N)$-palladacycles. In addition, NHC ligated palladacycles were investigated for their catalytic activity for Suzuki–Miyaura coupling of organic halides with phenylboronic acid. All complexes were fully characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

2. Results and discussion

2.1. Preparation of imidazolium salts (2a–c)

The preparation of imidazolium salts and their mononuclear palladacyclic complexes is shown in the Scheme. The imidazolium salts **2a**–**c** were obtained by the treatment of N-mesitylimidazole with benzyl bromide derivatives. The off-white solids (**2a**–**c**) were then recrystallized from ethanol and diethyl ether. The NMR spectral data are in agreement with the proposed structure. The ^{1}H NMR spectrum of the imidazolium salts displays a singlet proton signal at δ 10.38, 10.28, and 10.16 ppm, respectively. The ^{13}C NMR of imidazolium salts shows NCN sp^2 carbon signals at δ 141.1, 141.0, and 141.0 ppm as singlets, respectively. The benzylic methylene carbon signals for **2a**–**c** were observed between δ 5.89 and 5.93 ppm.



Reagents and conditions: **(i)** 2,4,6-trimethylbenzyl bromide (**3a**), 2,3,5,6-tetramethylbenzyl bromide (**3b**) or 2,3,4,5,6-pentamethylbenzyl bromide (**3c**), PhMe, 110 °C, 18 h;

(ii) $[Pd(ppy)(\mu\text{-OAc})]_2$, PhMe, 110 °C, 24 h.

Scheme. Synthesis of NHC ligands (**2**) and NHC-palladacyclic complexes (**3**).

2.2. Preparation of palladacyclic complexes (3a–c)

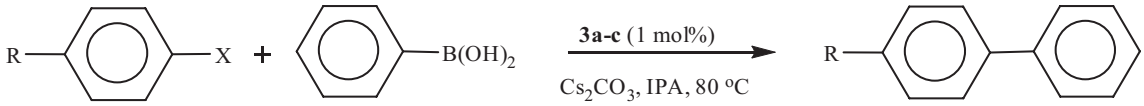
Mononuclear N-heterocyclic carbene-based palladacycles (**3a**–**c**) were obtained in the reaction of acetate-bridged dimeric palladacycle, $[Pd(\mu\text{-OAc})(ppy)]_2$ (ppy: 2-phenylpyridine), with a stoichiometric of the NHC precursors according to the Scheme. These complexes are stable towards air and moisture. The novel compounds were characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy. According to the ^{13}C NMR spectrum, the diagnostic Pd-N*C*N (**3a**–**c**) resonances appeared as singlets between δ 174.1 and 174.3 ppm. ^{13}C chemical shifts provide a useful diagnostic tool for this type of metal carbene complexes.

2.3. Catalytic studies

Cyclopalladated compounds are the most active catalysts for C–C and C–heteroatom bond-forming reactions among the catalysts reported. The true start of the field of palladacycles as catalysts in cross-coupling reactions occurred in 1995 with the introduction by Hermann and Beller of a new phosphine-bearing palladacycle.[21] Activity is not limited to palladium-phosphine complexes. Several N-donor palladacyclic complexes have been presented showing good activity.[22,23] We now report the activity of these catalysts, **3a**–**c**, in the Suzuki–Miyaura cross-coupling reaction. During the course of performing experiments on the catalytic dehalogenation of aryl bromides with **3a**–**c** (1×10^{-5} mol, 1 mol%) 2-propanol (3 mL) was used as the solvent and Cs_2CO_3 as base (1.5 equiv.)

We achieved very high yields of dehalogenated products at 80 °C (Table). The results indicated that NHC-bearing palladacyclic complexes exhibit excellent activity at low catalyst loadings when aryl bromides, both activated and unactivated, are used as substrates. Various 4-substituted aryl bromides, bearing either electron-withdrawing or electron-donating groups, provided the corresponding cross-coupling products in excellent yields (Table, entries 3, 5–9). For example, 4-bromoacetophenone was successfully coupled with phenylboronic acid providing a 97% yield in 30 min (Table, entry 9), which was more effective compared with the reported method.[24,25] The cross coupling of 4-bromoacetophenone and phenylboronic acid gave the product in 93% yield in 60 min (Table, entry 3). 4-Bromoacetophenone also coupled with phenylboronic acid, resulting in a 99% yield in 60 min (Table, entry 6). However, benzene with an electron-withdrawing group showed lower reactivity. The coupling reaction of bromobenzene with phenylboronic acid afforded a 36% yield of the product in 60 min (Table, entry 1). The reaction of 4-methlybenzene with electron-rich phenylboronic acid provided the heterobiaryl products with more than 90% yields (Table, entries 5 and 8). In the case of bromoacetophenone the corresponding products were obtained exclusively with high turnover frequencies (TOF) (Table, entries 3, 6, 9), but these values were lower compared with those of most homogeneous catalysts.

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



Entry	Pd-NHC	[Pd] (%)	Ar-X	T (°C)	t (min)	Yield (%)[b,c]	TOF (h^{-1})[d]
1	**3a**	1	Ph-Br	80	60	36	18.0
2	**3a**	1	Me-C_6H_4-4-Br	80	60	18	9.0
3	**3a**	1	CH_3(O)C-C_6H_4-4-Br	80	60/30	93/66	46.5/55.0
4	**3b**	1	Ph-Br	80	60	47	23.5
5	**3b**	1	Me-C_6H_4-4-Br	80	60	99	49.5
6	**3b**	1	CH_3(O)C-C_6H_4-4-Br	80	60/30	99/85	49.5/85.0
7	**3c**	1	Ph-Br	80	60	99	49.5
8	**3c**	1	Me-C_6H_4-4-Br	80	60	99	49.5
9	**3c**	1	CH_3(O)C-C_6H_4-4-Br	80	60/30	99/97	49.5/97.0
10	**3c**	1	CH_3(O)C-C_6H_4-4-Cl	80	240/480	65/67	8.1/4.2

[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. [d] Referred to the reaction time indicated in column; TOF = (mol product/mol Pd(II) cat.) $\times$ h^{-1}.

These results showed that this catalytic system (**3c**) could tolerate aryl bromides with both electron-withdrawing and electron-rich groups, and the electronic effect had little influence on the reactivity of the aryl bromides.

Furthermore, the activity of the catalysts in the cross-coupling reaction of aryl chloride was tested. **3c** and 4-chloroacetophenone were selected as a catalyst and a model substrate for the catalytic test, respectively. However, the catalyst (**3c**) was less effective for coupling aryl chloride. As a result, activity (using 1 mol% catalysts) was acceptable for activated aryl bromides, but the activity for deactivated substrates was low. In addition, the activity for aryl chloride was much lower (Table, entry 10) than that mentioned above.

3. Conclusion

In summary, we were interested in an approach that would combine the important donating properties of NHC with the stability imparted by the palladacycle framework. To achieve this, a series of NHC-palladacycles derived from imidazolium precursors were synthesized and characterized. In addition, we also tested their catalytic activities in the Suzuki–Miyaura cross-coupling reaction. These palladacycles have been proven to be highly efficient catalysts for the Suzuki–Miyaura coupling of aryl bromides with phenylboronic acid. Reactions reach completion in short reaction times. The results indicate that the activity largely depends on the nature of N-substituents of the complexes **3a**–**c**. The complex **3c** shows the most noticeable activity and a maximum yield of 99% was achieved after 60 min.

4. Experimental

4.1. General procedures

All reactions for the preparations of **3a**–**c** were carried out under argon in flame-dried glassware using a standard Schlenk-type flask. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. Acetate-bridged palladium dimer, $[Pd(\mu\text{-}OAc)(ppy)]_2$ (ppy: 2-phenylpyridine),[26] and N-(2,4,6-trimethylphenyl)-1*H*-imidazole, **1**,[27] were prepared according to the literature, and ^1H and ^{13}C NMR measurement was performed using a Varian Mercury AS 400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts (δ) are relative to TMS. Catalytic studies were performed using a gas chromatograph (HP, Agilant-6890N). Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. Elemental analyses were performed by the TÜBİTAK (Ankara, Turkey) Microlab.

4.2. General procedure for the preparation of 2a–c

The benzyl bromide derivative[28] (2,4,6-trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide or 2,3,4,5,6-pentamethylbenzyl bromide) (2.0 mmol) and N-(2,4,6-trimethylphenyl)-1*H*-imidazole (**1**, 2.0 mmol) were refluxed in toluene (10.0 mL) at 110 °C for 18 h. The volume of the solution was reduced to 5.0 mL; diethyl ether was added to the remaining solution, which was vigorously shaken and then decanted. The solid residue was washed with diethyl ether (3.0 × 20.0 mL) to obtain a white solid, which was recrystallized from CH_2Cl_2/Et_2O (3.0 mL/15.0 mL).

4.2.1. N-(2,4,6-trimethylphenyl)-N'-(2,4,6-trimethylbenzyl)imidazolium bromide (2a)

Yield: 0.64 g (80%), mp 274–276 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 6H, $C_6H_2(CH_3)_3$-*o*-CH_3); 2.24 (s, 3H, $C_6H_2(CH_3)_3$-*p*-CH_3); 2.28 (s, 9H, $NCH_2C_6H_2(CH_3)_3$); 5.91 (s, 2H, $NCH_2C_6H_2(CH_3)_3$); 6.88

(s, 2H, $C_6H_2(CH_3)_3$); 6.93 (s, 2H, $NCH_2C_6H_2(CH_3)_3$); 7.16 (s, 1H, NC*H*CHN); 7.20 (s, 1H, NCHC*H*N); 10.38 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.5 ($C_6H_2(CH_3)_3$-*o*-*C*H$_3$); 19.7 ($C_6H_2(CH_3)_3$-*p*-*C*H$_3$); 20.8 ($NCH_2C_6H_2(CH_3)_3$-*o*-*C*H$_3$); 20.9 ($NCH_2C_6H_2(CH_3)_3$-*p*-*C*H$_3$); 48.4 (N*C*H$_2$C$_6$H$_2$(CH$_3$)$_3$); 121.6 (N*C*HCHN); 123.4 (NCH*C*HN); 125.5 ($C_6H_2(CH_3)_3$); 129.7 ($C_6H_2(CH_3)_3$); 129.8 ($C_6H_2(CH_3)_3$); 130.4 ($C_6H_2(CH_3)_3$); 134.0 ($NCH_2C_6H_2(CH_3)_3$); 137.2 ($NCH_2C_6H_2(CH_3)_3$); 138.0 ($NCH_2C_6H_2(CH_3)_3$); 139.7 ($NCH_2C_6H_2(CH_3)_3$); 141.1 (N*C*HN). Elemental analyses (%) calc. for $C_{22}H_{27}BrN_2$: C, 66.16; H, 6.81; N, 7.01; found: C, 66.06; H, 6.75; N, 6.96.

4.2.2. N-(2,4,6-trimethylphenyl)-N'-(2,3,5,6-tetramethylbenzyl)imidazolium bromide (2b)

Yield: 0.66 g (80%), mp 282–283 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 6H, $C_6H_2(CH_3)_3$-*o*-C*H*$_3$); 2.16 (s, 12H, $NCH_2C_6H(CH_3)_4$-*o*,*m*-C*H*$_3$); 2.24 (s, 3H, $C_6H_2(CH_3)_3$-*p*-C*H*$_3$); 5.93 (s, 2H, NC*H*$_2$C$_6$H(CH$_3$)$_4$); 6.89 (s, 2H, $C_6H_2(CH_3)_3$); 6.97 (s, 1H, $NCH_2C_6H(CH_3)_4$); 7.13 (s, 1H, NC*H*CHN); 7.25 (s, 1H, NCHC*H*N); 10.28 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.6 ($C_6H_2(CH_3)_3$-*o*-*C*H$_3$); 17.4 ($C_6H_2(CH_3)_3$-*p*-*C*H$_3$); 20.2 ($NCH_2C_6H(CH_3)_4$-*o*-*C*H$_3$); 20.8 ($NCH_2C_6H(CH_3)_4$-*m*-*C*H$_3$); 49.0 (N*C*H$_2$C$_6$H(CH$_3$)$_4$); 121.6 (N*C*HCHN); 123.5 (NCH*C*HN); 128.2 ($C_6H(CH_3)_4$); 129.6 ($C_6H(CH_3)_4$); 130.4 ($C_6H(CH_3)_4$); 133.2 ($C_6H(CH_3)_4$); 133.8 ($NCH_2C_6H(CH_3)_4$); 133.9 ($NCH_2C_6H(CH_3)_4$); 134.7 ($NCH_2C_6H(CH_3)_4$); 137.0 ($NCH_2C_6H(CH_3)_4$); 141.0 (N*C*HN). Elemental analyses (%) calc. for $C_{23}H_{29}BrN_2$: C, 66.82; H, 7.07; N, 6.78; found: C, 66.71; H, 6.95; N, 6.85.

4.2.3. N-(2,4,6-trimethylphenyl)-N'-(2,3,4,5,6-pentamethylbenzyl)imidazolium bromide (2c)

Yield: 0.73 g (85%), mp 292–294 °C. ^{1}H NMR (400 MHz, DMSO): δ = 1.96 (s, 6H, $C_6H_2(CH_3)_3$-*o*-C*H*$_3$); 2.13 (s, 6H, $NCH_2C_6(CH_3)_5$-*o*-C*H*$_3$); 2.16 (s, 3H, $C_6H_2(CH_3)_3$-*p*-C*H*$_3$); 2.18 (s, 6H, $NCH_2C_6(CH_3)_5$-*m*-C*H*$_3$); 2.22 (s, 3H, $NCH_2C_6(CH_3)_5$-*p*-C*H*$_3$); 5.89 (s, 2H, NC*H*$_2$C$_6$(CH$_3$)$_5$); 6.86 (s, 2H, $C_6H_2(CH_3)_3$); 7.16 (s, 1H, NC*H*CHN); 7.28 (s, 1H, NCHC*H*N); 10.16 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.6 ($C_6H_2(CH_3)_3$-*o*-*C*H$_3$); 16.7 ($C_6H_2(CH_3)_3$-*p*-*C*H$_3$); 17.1 ($NCH_2C_6(CH_3)_5$-*o*-*C*H$_3$); 17.6 ($NCH_2C_6(CH_3)_5$-*m*-*C*H$_3$); 20.9 ($NCH_2C_6(CH_3)_5$-*p*-*C*H$_3$); 49.6 (N*C*H$_2$C$_6$(CH$_3$)$_5$); 121.8 (N*C*HCHN); 123.3 (NCH*C*HN); 125.6 ($C_6H_2(CH_3)_3$); 129.6 ($C_6H_2(CH_3)_3$); 130.5 ($C_6H_2(CH_3)_3$); 133.4 ($C_6H_2(CH_3)_3$); 133.6 ($NCH_2C_6(CH_3)_5$); 134.0 ($NCH_2C_6(CH_3)_5$); 136.9 ($NCH_2C_6(CH_3)_5$); 137.1 ($NCH_2C_6(CH_3)_5$); 141.0 (N*C*HN). Elemental analyses (%) calc. for $C_{24}H_{31}BrN_2$: C, 67.44; H, 7.31; N 6.55; found: C, 67.55; H, 7.83; N, 6.78.

4.3. General procedure for the preparations of 3a–c

A sample of $[Pd(\mu\text{-}OAc)_2(ppy)]_2$ (0.23 mmol) was refluxed with one of the compounds of type **2a**–**c** (0.46 mmol) in dry toluene (10.0 mL) at 110 °C for 24 h. The solvent was removed in vacuo, the remaining precipitate was then dissolved in dichloromethane (2.0 mL), and recrystallization from CH_2Cl_2/Et_2O afforded the complexes of type **3a**–**c** (2.0 mL/10.0 mL).

4.3.1. Bromo[N-(2,4,6-trimethylphenyl)-N'-(2,4,6-trimethylbenzyl)imidazol-2-yliden][2-{2-pyridyl}phenyl]palladium(II) (3a)

Yield: 0.08 g (50%), mp 250–251 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (s, 6H, $C_6H_2(CH_3)_3$-*o*-C*H*$_3$); 2.23 (s, 6H, $NCH_2C_6H_2(CH_3)_3$-*o*-C*H*$_3$); 2.30 (s, 3H, $C_6H_2(CH_3)_3$-*p*-C*H*$_3$); 2.33 (s, 3H, $NCH_2C_6H_2(CH_3)_3$-

p-CH_3); 5.25 (d, 1H, J = 14.5 Hz, NCHHC$_6$H$_2$(CH$_3$)$_3$); 6.01 (d, 1H, J = 14.1 Hz, NCHHC$_6$H$_2$(CH$_3$)$_3$); 6.46 (d, 2H, J = 7.4 Hz, C$_6H_2$(CH$_3$)$_3$); 6.57 (d, 1H, J = 2.0 Hz, NCHCHN); 6.79 (br, 1H, Ar-CH); 6.84 (d, 1H, J = 2.0 Hz, NCHCHN); 6.93 (br, 1H, Ar-CH); 6.93 (s, 2H, NCH$_2$C$_6H_2$(CH$_3$)$_3$); 6.99 (m, 1H, Ar-CH); 7.08 (t, 1H, J = 7.6 Hz, Ar-CH); 7.53 (d, 1H, J = 6.7 Hz, pyridyl-CH); 7.64 (d, 1H, J = 7.8 Hz, pyridyl-CH); 7.70 (m, 1H, pyridyl-CH); 9.46 (d, 1H, J = 5.5 Hz, pyridyl-CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.68 (C$_6$H$_2$(CH$_3$)$_3$-*o*-CH$_3$); 19.72 (C$_6$H$_2$(CH$_3$)$_3$-*p*-CH$_3$); 20.12 (NCH$_2$C$_6$H$_2$(CH$_3$)$_3$-*o*-CH$_3$); 21.04 (NCH$_2$C$_6$H$_2$(CH$_3$)$_3$-*p*-CH$_3$); 50.14 (NCH$_2$C$_6$H$_2$(CH$_3$)$_3$); 117.85 (NCHCHN); 119.23 (NCHCHN); 122.11 (Ar-C); 123.22 (Ar-C); 123.59 (Ar-C); 123.97 (Ar-C); 127.88 (Ar-C); 128.78 (C_6H$_2$(CH$_3$)$_3$); 129.07 (Ar-C); 129.33 (Ar-C); 129.48 (C_6H$_2$(CH$_3$)$_3$); 134.64 (C_6H$_2$(CH$_3$)$_3$); 135.72 (C_6H$_2$(CH$_3$)$_3$); 137.03 (Ar-C); 137.27 (Ar-C); 138.05 (Ar-C); 138.69 (pyridyl-CH); 146.79 (pyridyl-CH); 151.41 (pyridyl-CH); 155.81 (pyridyl-CH); 164.19 (pyridyl-CH); 174.3 (Pd-$C_{carbene}$). Elemental analyses (%) calc. for C$_{33}$H$_{34}$BrN$_3$Pd: C, 60.15; H, 5.20; N, 6.38; found: C, 59.23; H, 4.74; N, 6.01.

4.3.2. Bromo[N-(2,4,6-trimethylphenyl)-N'-(2,3,5,6-tetramethylbenzyl)imidazol-2-yliden][2-{2-pyridyl}phenyl]palladium(II) (3b)

Yield: 0.09 g (55%), mp 265–266 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.04 (s, 6H, C$_6$H$_2$(CH$_3$)$_3$-*o*-CH_3); 2.24 (s, 6H, NCH$_2$C$_6$H(CH$_3$)$_4$-*o*-CH_3); 2.25 (s, 6H, NCH$_2$C$_6$H(CH$_3$)$_4$-*m*-CH_3); 2.26 (s, 3H, C$_6$H$_2$(CH$_3$)$_3$-*p*-CH_3); 5.35 (d, 1H, J = 14.8 Hz, NCHHC$_6$H(CH$_3$)$_4$); 6.07 (d, 1H, J = 14.4 Hz, NCHHC$_6$H(CH$_3$)$_4$); 6.50 (dd, 2H, J^1 = 7.4 Hz, J^2 = 1.2 Hz, C$_6H_2$(CH$_3$)$_3$); 6.57 (d, 1H, J = 2.0, NCHCHN); 6.78 (br, 1H, Ar-CH); 6.83 (d, 1H, J = 2.0 Hz, NCHCHN); 6.93 (br, 1H, Ar-CH); 6.99 (dd, 1H, J^1 = 7.4 Hz, J^2 = 1.6 Hz, Ar-CH); 7.02 (s, 1H, NCH$_2$C$_6H$(CH$_3$)$_4$); 7.06–7.10 (m, 1H, Ar-CH); 7.53 (dd, 1H, J^1 = 7.6 Hz, J^2 = 1.4 Hz, pyridyl-CH); 7.63 (d, 1H, J = 8.2 Hz, pyridyl-CH); 7.69 (td, 1H, J^1 = 7.7 Hz, J^2 = 1.8 Hz, pyridyl-CH); 9.47 (dd, 1H, J^1 = 4.9 Hz, J^2 = 1.0 Hz, pyridyl-CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.97 (C$_6$H$_2$(CH$_3$)$_3$-*o*-CH$_3$); 19.67 (C$_6$H$_2$(CH$_3$)$_3$-*p*-CH$_3$); 20.46 (NCH$_2$C$_6$H(CH$_3$)$_4$-*o*-CH$_3$); 21.01 (NCH$_2$C$_6$H(CH$_3$)$_4$-*m*-CH$_3$); 50.86 (NCH$_2$C$_6$H(CH$_3$)$_4$); 117.85 (NCHCHN); 119.56 (NCHCHN); 122.08 (Ar-C); 123.05 (Ar-C); 123.60 (Ar-C); 123.97 (Ar-C); 128.75(Ar-C); 129.03 (Ar-C); 129.45 (Ar-C); 130.64 (C_6H$_2$(CH$_3$)$_3$); 132.34 (C_6H$_2$(CH$_3$)$_3$); 134.24 (C_6H$_2$(CH$_3$)$_3$); 134.66 (C_6H$_2$(CH$_3$)$_3$); 137.05 (Ar-C); 137.30 (Ar-C); 138.05 (Ar-C); 138.59 (pyridyl-CH); 146.79 (pyridyl-CH); 151.35 (pyridyl-CH); 155.77 (pyridyl-CH); 164.14 (pyridyl-CH); 174.16 (Pd-$C_{carbene}$). Elemental analyses (%) calc. for C$_{34}$H$_{36}$BrN$_3$Pd: C, 60.68; H, 5.39; N, 6.24; found: C, 58.74; H, 5.41; N, 5.85.

4.3.3. Bromo[N-(2,4,6-trimethylphenyl)-N'-(2,3,4,5,6-pentamethylbenzyl)imidazol-2-yliden][2-{2-pyridyl}phenyl]palladium(II) (3c)

Yield: 0.08 g (50%), mp 275–276 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.04 (s, 6H, C$_6$H$_2$(CH$_3$)$_3$-*o*-CH_3); 2.22 (s, 6H, NCH$_2$C$_6$(CH$_3$)$_5$-*o*-CH_3); 2.25 (s, 6H, NCH$_2$C$_6$(CH$_3$)$_5$-*m*-CH_3); 2.27 (s, 3H, C$_6$H$_2$(CH$_3$)$_3$-*p*-CH_3); 2.30 (s, 3H, NCH$_2$C$_6$(CH$_3$)$_5$-*p*-CH_3); 5.36 (d, 1H, J = 14.8 Hz, NCHHC$_6$(CH$_3$)$_5$); 6.07 (d, 1H, J = 14.8 Hz, NCHHC$_6$(CH$_3$)$_5$); 6.50 (d, 2H, J = 7.4 Hz, C$_6H_2$(CH$_3$)$_3$); 6.61 (d, 1H, J = 2.0 Hz, NCHCHN); 6.77 (br, 1H, Ar-CH); 6.82 (d, 1H, J = 2.0 Hz, NCHCHN); 6.93 (br, 1H, Ar-CH); 6.98–7.09 (m, 2H, Ar-CH); 7.51 (dd, 1H, J^1 = 7.8 Hz, J^2 = 1.2 Hz, pyridyl-CH); 7.60 (d, 1H, J = 7.8 Hz, pyridyl-CH); 7.66 (td, 1H, J^1 = 7.6 Hz, J^2 = 1.6 Hz, pyridyl-CH); 9.46 (d, 1H, J = 5.5 Hz, pyridyl-

CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.79 ($C_6H_2(CH_3)_3$-o-CH_3); 16.94 ($NCH_2C_6(CH_3)_5$-o-CH_3); 17.07 ($NCH_2C_6(CH_3)_5$-m-CH_3); 19.63 ($C_6H_2(CH_3)_3$-p-CH_3); 20.97 ($NCH_2C_6(CH_3)_5$-p-CH_3); 51.39 ($NCH_2C_6(CH_3)_5$); 117.84 (NCHCHN); 119.68 (NCHCHN); 122.01 (Ar-C); 122.94 (Ar-C); 123.61 (Ar-C); 123.94 (Ar-C); 128.06 (Ar-C); 128.73 (Ar-C); 128.99 (Ar-C); 129.44 ($C_6H_2(CH_3)_3$); 134.20 ($C_6H_2(CH_3)_3$); 134.59 ($C_6H_2(CH_3)_3$); 135.81 ($C_6H_2(CH_3)_3$); 137.09 (Ar-C); 137.33 (Ar-C); 138.02 (Ar-C); 138.54 (pyridyl-CH); 146.79 (pyridyl-CH); 151.33 (pyridyl-CH); 155.78 (pyridyl-CH); 164.17 (pyridyl-CH); 174.08 (Pd-$C_{carbene}$). Elemental analyses (%) calc. for $C_{35}H_{38}BrN_3Pd$: C, 61.19; H, 5.58; N, 6.12; found: C, 61.30; H, 5.69; N, 6.01.

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