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C–H Bond Activation of Palladium Complexes That Feature Pendant Benzamidinate Ligands and Their Catalytic Behaviours

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The pendant benzamidines {Ph–C[=N–(2,6-di-*i*Pr-C_6H_3)]-(NH^E)} [^E = $(CH_2)_2NMe_2$, CH_2Py] and their palladium complexes [(Ph–C{=N^E}{NH–(2,6-di-*i*Pr-C_6H_3)})$Pd(OAc)_2$] [^E = $(CH_2)_2NMe_2$ (**1**), CH_2Py (**2**)] have been prepared. Upon heating, the corresponding palladacyclic complexes, [({η^1-C_6H_4}–C(=N^E){NH–(2,6-di-*i*Pr-C_6H_3)})PdOAc] [^E = $(CH_2)_2$-NMe_2 (**3**), CH_2Py (**4**)], were obtained. Due to the substituent groups on the *ortho* positions of the phenyl ring attached to the nitrogen atom of the amidinate group, the C–H bond activation process was observed on the *ortho* position of the phenyl ring attached to the carbon atom of the amidinate group. This process can be proved by X-ray structural determination. The molecular structures are reported for compounds **1** and **4**. Catalytic application of cyclopalladated derivatives **3** and **4** toward the Suzuki reaction was also investigated.

Introduction

C–H bond activation is a well-known process by means of oxidative addition or electrophilic substitution reactions to afford cyclometalated complexes. Cyclometalated complexes play important roles in modern organometallic chemistry, such as organic synthesis, asymmetric synthesis and photochemistry.[1,2] These processes predominantly focus on the second- and third-row transition metals with N-donor ligands.[1,2] The mechanistic investigations of these reactions have been studied with respect to ligand precursors precoordinated to the metal centre followed by arrangement of the ligand precursors to allow for C–H bond activation.[3] Although cyclometalation reactions on palladium(II) complexes have been thoroughly studied by a number of research groups, not many of these processes are known to result in isolation of the corresponding organometallic complexes.[4–7]

In our previous report,[8] we used molecular structures to demonstrate that the cyclometalation reaction happened at the *ortho* position of the phenyl ring attached to the nitrogen atom rather than at the *ortho* position of the phenyl ring attached to the carbon atom of the amidine function. A plausible mechanism for this process has been reported by us. However, the palladium chelate complexes that could be precursors for cyclometalation reactions cannot be isolated easily due to the quick cyclometalation process. To prove this plausible mechanism, the *ortho*-hydrogen atoms of the phenyl ring attached to the nitrogen atom of the amidine function were substituted with *i*Pr groups to prevent the *ortho*-metalation of the palladium chelate complex. Thus the isolation of precursors for the cyclometalation reaction might be achieved. In this paper, we present benzamidinate ligand precursors with bulkier substituents to study how the cyclometalation steps take place. The application of palladacyclic complexes to a Suzuki reaction is also examined.

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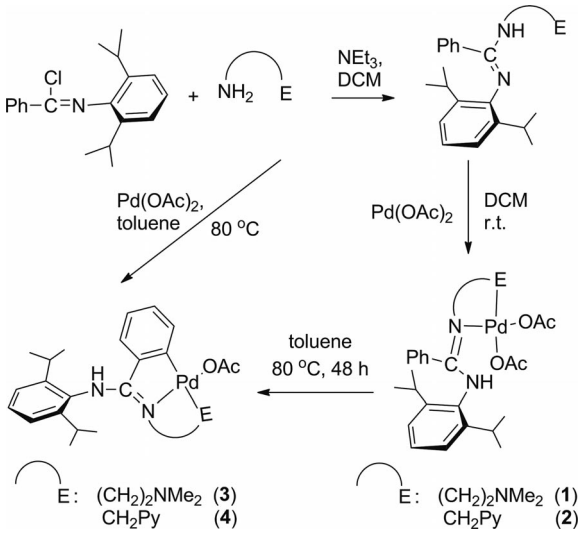
Results and Discussion

Synthesis of Benzamidinates Ligand Precursors and Pd Complexes

The desired *N*,*N*′-disubstituted benzamidines were prepared according to a method similar to our previous report.[8] Treatment of *N*-(2,6-diisopropylphenyl)benzimidoyl chloride[9a] with the corresponding amines (1 molar equiv.) in the presence of triethylamine affords benzamidines {Ph–C[=N–(2,6-di-*i*Pr-C_6H_3)](NH^E)} (^E = $(CH_2)_2NMe_2$, CH_2Py) in moderate yield. *N*-(2,6-Diisopropylphenyl)-*N*′-(2-dimethylaminoethyl)benzamidine has already been reported.[9b,9c] *N*-(2,6-Diisopropylphenyl)-*N*′-(2-methylpyridine)benzamidine was characterized by NMR spectroscopy as well as elemental analyses. Due to the tautomeric rotation of amidine, complex and broad signals were found in the ^{1}H NMR spectrum. Therefore high-temperature NMR spectroscopic data are reported in the Exp. Section for *N*-(2,6-diisopropylphenyl)-*N*′-(2-methylpyridine)benzamidine. Treatment of benzamidines with $Pd(OAc)_2$ (1 molar equiv.) in dichloromethane afforded palladium chelate complexes **1** or **2**. The gradual formation of the corresponding cyclometalated compound **3** was observed upon standing compound **1** in a solution of [D]chloroform at room temperature for a couple of days with an upfield shift of the N*H* peak and the loss of one –OAc peak in the ^{1}H NMR spectrum. The

syntheses of palladacyclic complexes **3** and **4** were achieved by heating **1** in toluene or **2** in THF at 80 °C. Complexes **3** and **4** can also be prepared by an alternative route by means of direct reactions of benzamidines with $Pd(OAc)_2$ in toluene at 80 °C. Complexes **1**–**4** were characterized by NMR spectroscopy as well as elemental analyses. A summary of the syntheses and proposed structures of palladium complexes is shown in Scheme 1.



Scheme 1. Preparation of palladium complexes **1**–**4**.

In each palladium chelate complex, one N*H* singlet around δ = 10 ppm (δ = 9.99 ppm for **1**; 10.20 ppm for **2**) and two peaks that correspond to –OAc groups were found in the ^{1}H NMR spectrum. For each palladacyclic complex, the N*H* singlet moved upfield (δ = 6.67 ppm for **3**; 6.83 ppm for **4**) and only one peak that corresponded to the –OAc group appeared around δ = 2 ppm (δ = 2.11 ppm for **3**; 2.21 ppm for **4**) in the ^{1}H NMR spectra, which indicates that the carbon metalation of the phenyl group might happen instead of N*H* deprotonation with the release of one molar equivalent of HOAc, as shown in Figures 1 and 2.

Suitable crystals of **1** for X-ray refinement were grown from a solution of dichloromethane/hexane. The molecular structure is depicted in Figure 3. The bond angles [from 84.02(10) to 96.86(9)°] around the palladium metal centre can be described as a slightly distorted square planar with two *cis*-oriented nitrogen atoms from the benzamidinate ligand and two oxygen atoms from two –OAc groups. The chelate ring of complex **1** is nearly coplanar with the torsion angle O(1)–O(3)–N(3)–N(2) = 1.3°. The bond lengths of $Pd–N_{amine}$ [2.042(3) Å] and $Pd–N_{imine}$ [2.042(3) Å] are within those [2.044(4)–2.0683(19) Å for $Pd–N_{amine}$; 1.991(2)–2.050(2) Å for $Pd–N_{imine}$] found in palladium N,N′-chelate complexes.[7b] The bond lengths of $Pd–O_{OAc}$ [2.021(2) and 2.032(2) Å] are close to those [1.983(4)–2.029(2) Å] found in palladium acetate complexes.[7b,10f] The C–N bond lengths of the NCN moiety are not equal with 1.337(4) and 1.308(4) Å, respectively, thus indicating

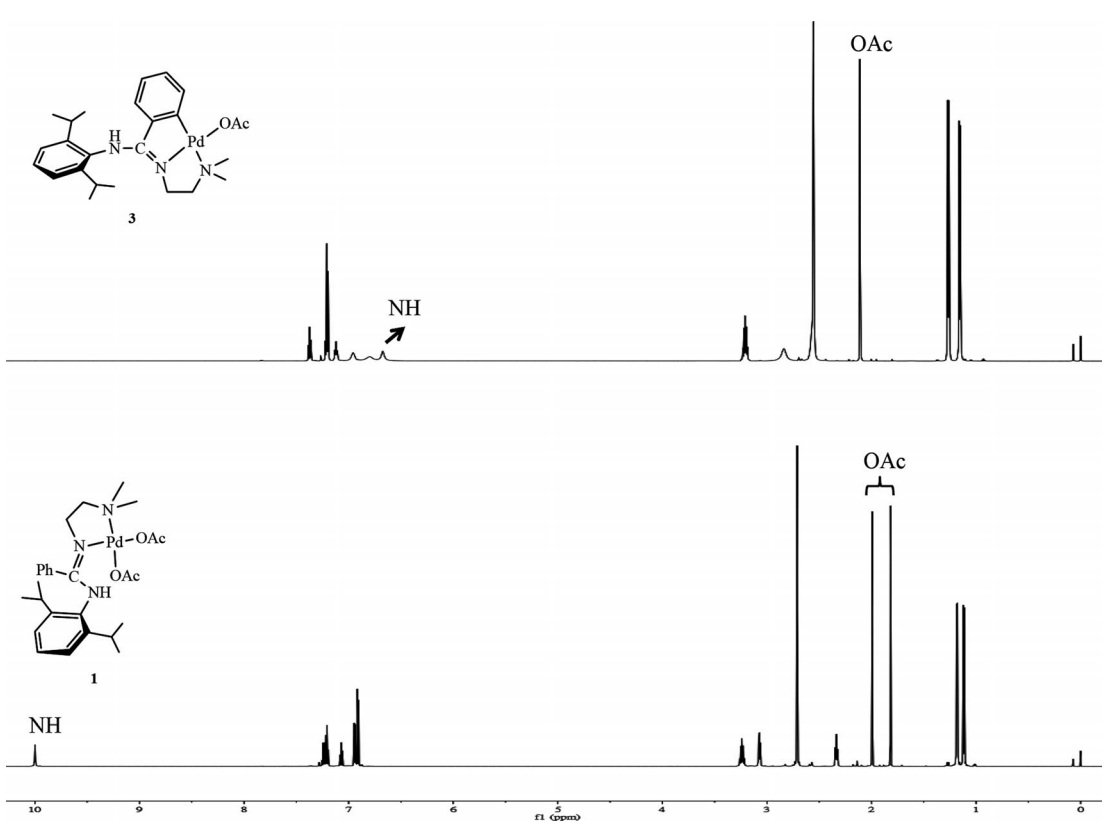


Figure 1. ^{1}H NMR spectra in $CDCl_3$ for **1** (bottom) and **3** (top).

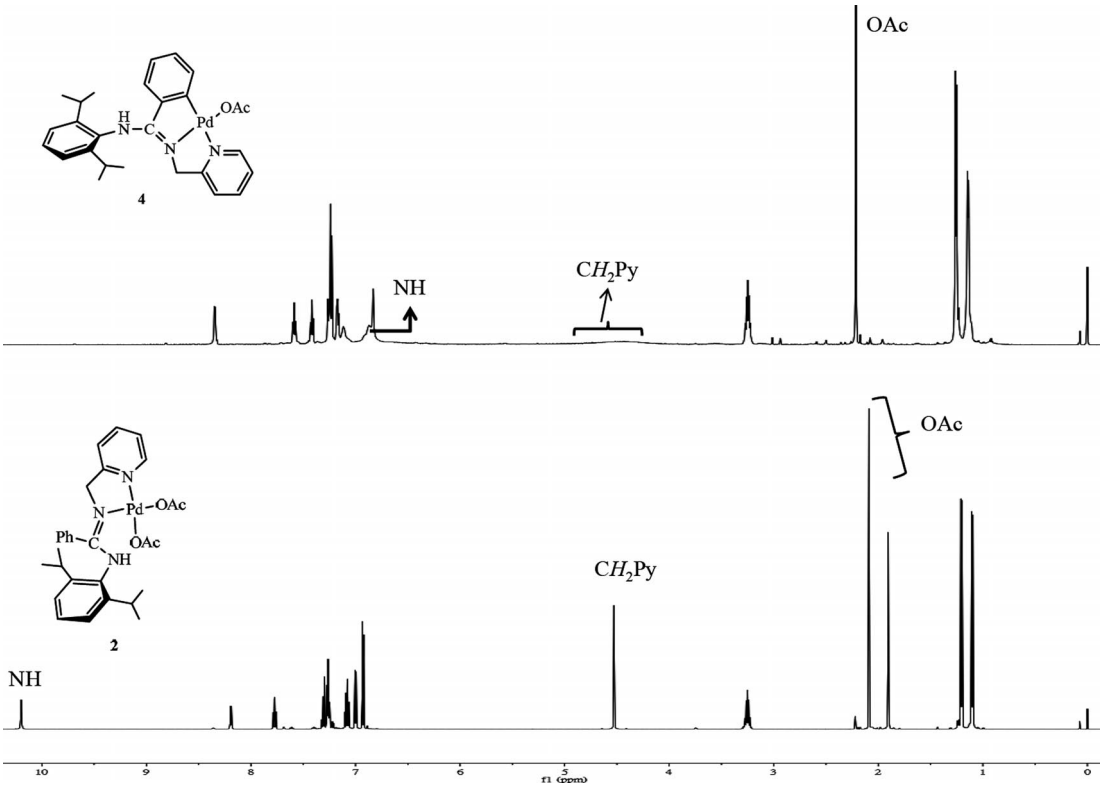


Figure 2. ^{1}H NMR spectra in $CDCl_3$ for **2** (bottom) and **4** (top).

the localized nature of the imine C=N and amine C–N bonds and the 1,3-shift of a proton from the nitrogen atom of the amine group to the nitrogen atom of the imine group on going from the free ligand to the mononuclear CNN cyclopalladated compound. On the basis of the molecular structure of **1**, the *ortho* substituents actually prevent the palladium chelate complexes from taking part in cyclometalation (Scheme 2) to form a six-membered metallacycle and prove the existence of palladacyclic precursors in the previously proposed mechanism.[8]

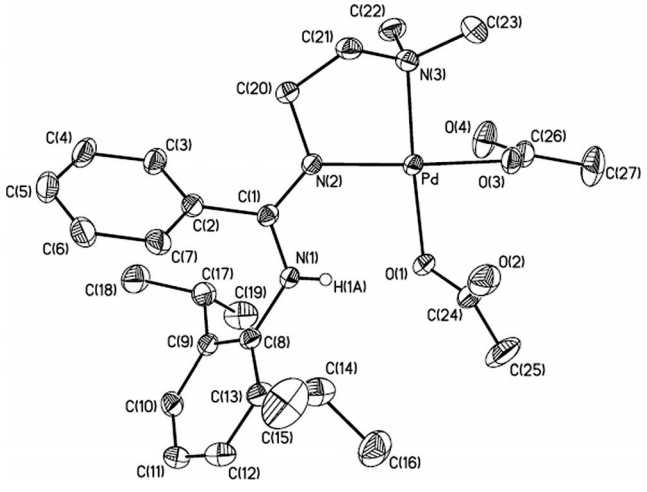
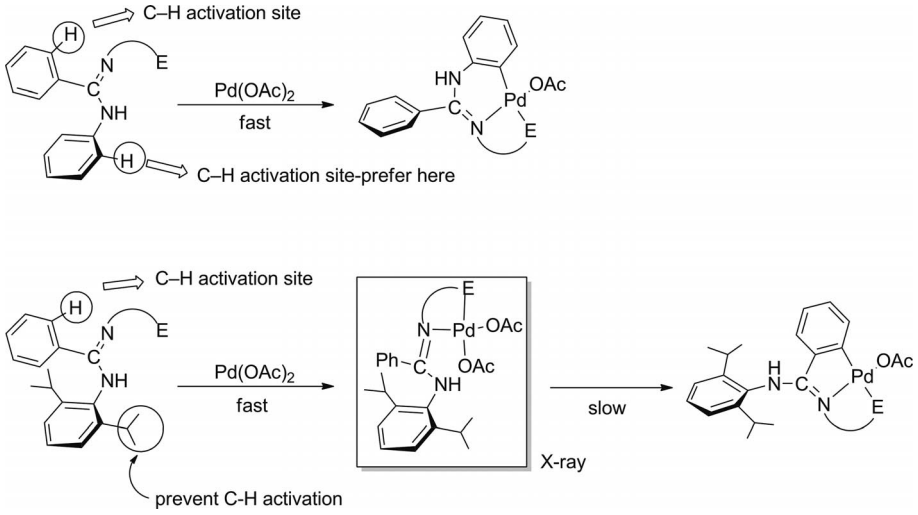


Figure 3. Molecular structure of **1**. Selected bond lengths [Å] and bond angles [°]: Pd–O(1) 2.032(2), Pd–O(3) 2.021(2), Pd–N(2) 2.042(2), Pd–N(3) 2.042(3), C(1)–N(2) 1.308(4), C(1)–N(1) 1.337(4), N(1)–C(8) 1.439(4); N(2)–Pd–O(1) 96.86(9), N(3)–Pd–O(3) 92.99(11), N(2)–Pd–N(3) 84.14(11), O(3)–Pd–O(1) 84.02(10), O(1)–Pd–N(3) 177.00(11), O(3)–Pd–N(2) 176.67(10). Hydrogen atoms on carbon atoms omitted for clarity.

Suitable crystals of **4** for X-ray refinement were grown from concentrated chloroform solution. The molecular structure is depicted in Figure 4. The bond angles [from 81.54(9) to 99.32(9)°] around the palladium metal centre indicate a complex that has a slightly distorted square-planar geometry, in which the palladium metal centre is coordinated with one pyridine nitrogen atom, one imine nitrogen atom, one metalated carbon atom, and one acetate oxygen atom to form two five-membered metallacycles. The bond lengths of Pd–N_{py} [2.113(2) Å] and Pd–$C_{metalated}$ [1.978(3) Å] are within those [1.964(3)–2.150(3) Å for Pd–N_{py}; 1.961(4)–2.078(2) Å for Pd–$C_{metalated}$] found in metalated palladacycles.[10,11] The bond length of Pd–O_{OAc} [2.0545(16) Å] are within those [2.036(2)–2.126(3) Å] found in palladacycles.[8,10f,10g,11] The bond length of Pd–$N_{C=N}$ [1.9606(19) Å] is close to those [1.981(3)–2.0321(18) Å] found in palladacycles.[8,10f,10g,11] The C–N bond lengths of the NCN moiety in **4** are not equal [1.304(3) Å for imine C(1)=N(2) and 1.351(3) Å for amine C(1)–N(1)], thereby indicating the localized nature of the imine C=N and amine C–N bonds. On the basis of the molecular structure of **4**, the cyclometalation reaction happens on the *ortho* position of the phenyl ring attached to the carbon atom of the NCN part to form a five-membered metallacycle as mononuclear palladium complex **4** rather than a dinuclear species.[7b] No aliphatic C–H activation product was obtained in this system.[6] Compared with the results reported previously,[8] for-



Scheme 2. Bulkier group on the *ortho* positions prevent the palladium chelate complexes from cyclometalation.

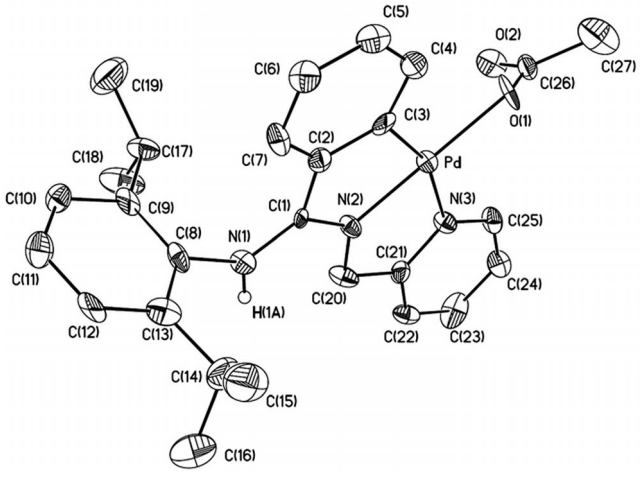


Figure 4. Molecular structure of **4**. Selected bond lengths [Å] and bond angles [°]: Pd–C(3) 1.978(3), Pd–O(1) 2.0545(16), Pd–N(2) 1.9606(19), Pd–N(3) 2.113(2), C(1)–N(1) 1.351(3), C(1)–N(2) 1.304(3), C(8)–N(1) 1.442(3); N(2)–Pd–C(3) 81.54(9), N(2)–Pd–N(3) 81.78(8), N(3)–Pd–O(1) 97.42(7), C(3)–Pd–O(1) 99.32(9), C(3)–Pd–N(3) 163.24(9), N(2)–Pd–O(1) 172.10(8). Hydrogen atoms on carbon atoms omitted for clarity.

mation of six-membered metallacycle through an aromatic C–H activation seems to be faster than that of a five-membered metallacycle. Once the *ortho* position of the phenyl ring is blocked from forming a six-membered metallacycle, an aromatic C–H activation might happen on the *ortho* position of the phenyl ring to form a five-membered metallacycle in this palladium pendant benzamidinate system.

Catalytic Studies for the Suzuki Reaction

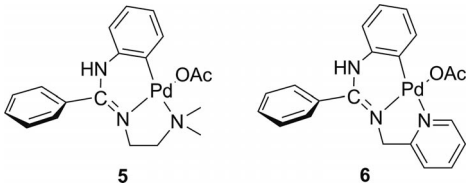
With the aim of demonstrating the catalytic activities of palladacycles that contain CNN-type ligands,[8,10f,10g,12] complexes **3** and **4** were introduced into the Suzuki coupling reaction.[13] To examine the catalytic activity, conditions that employ the coupling of 4-bromoanisole with phenylboronic acid (1.5 equiv.) catalyzed by **3** or **4** (1 mol-%) in the presence of base (3 equiv.) at 60 °C within 2 h were conducted. The optimum solvent/base mixture for the reaction was found to be toluene/K_3PO_4 after several trials with a combination of solvents (dimethylacetamide (DMA), THF and toluene) and base (KF, K_3PO_4 and Cs_2CO_3). Selected results are listed in Table 1. Poor conversion exhib-

Table 1. Suzuki coupling reaction catalyzed by palladium complexes (solvent: toluene).[a]

Entry	Catalyst	Aryl halide	Base	[Pd] [mol-%]	*T* [h]	Conversion [%][b]	Yield [%][c]
1[d]	**3**	4-bromoanisole	K_3PO_4	1	2	74	70
2[d]	**4**	4-bromoanisole	K_3PO_4	1	2	19	–
3[e]	**3**	4-bromoanisole	K_3PO_4	1	2	82	79
4[e]	**4**	4-bromoanisole	K_3PO_4	1	2	35	–
5[e]	**4**	4-bromoanisole	K_3PO_4	1	3	65	–
6	**3**	4-bromoanisole	K_3PO_4	10^{-3}	17	82	80
7	**3**	4-bromoanisole	K_3PO_4	10^{-5}	17	58	53
8	**3**	4-chloroacetophone	K_3PO_4	1	0.5	63	60
9	**3**	4-chloroacetophone	K_3PO_4	2	0.5	81	77
10	**3**	4-chloroacetophone	K_3PO_4	2	1	87	84
11	**4**	4-chloroacetophone	K_3PO_4	2	1	37	–
12[e]	**5**	4-bromoanisole	KF	1	3	72	65
13[e]	**6**	4-bromoanisole	K_3PO_4	1	3	84	75

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (3 mmol), toluene (3 mL), 100 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield (average of two experiments). [d] *T* = 60 °C. [e] *T* = 80 °C.

ited by **4** indicated that the catalytic activity of the complex with pendant amine functionality is better than that with pendant pyridine functionality in this system (Table 1, entries 1 and 2). A similar trend was observed by using less-reactive substrate 4-chloroacetophone with 2 mol-% palladium loading within 1 h at 100 °C (entries 10 and 11). Better conversion was observed by running reactions from 60 to 80 °C (entries 1 and 3). Because of the better activity and solubility of **3**, lower catalyst concentrations were investigated using catalyst/substrate ratios from 10^{-5} to 10^{-7} with 4-bromoanisole as substrate. The reactions gave conversion of 82% within 17 h for the 10^{-5} ratio, and 58% within 17 h for the 10^{-7} ratio at 100 °C (entries 6 and 7). Catalytic activity of **3** was tested by using less-reactive 4-chloroacetophenone as substrate with 1 mol-% palladium loading at 100 °C (entry 8). The reaction gave a conversion of 63% within 0.5 h. Better conversions were found by increasing the palladium loading (entry 9) or extending the reaction time (entry 10). To compare the catalytic activity of palladacycles with similar coordination modes in our previous report,[8] palladacycles **5** and **6** (as shown in Scheme 3) were examined by the reaction of 4-bromoanisole with phenylboronic acid catalyzed by 1 mol-% palladium loading under optimized conditions at 80 °C (entries 3–5, 12 and 13). On the basis of these results, the catalytic activity of the five-membered palladacycle that resulted from cyclometalation at the *ortho* position of the phenyl ring attached to the carbon atom of the NCN amidine function seems to be better than that with the six-membered metallacycle that results from cyclometalation at the *ortho* position of the phenyl ring attached to the nitrogen atom of the NCN amidine function for the palladacycles with the NMe_2 pendant functionality (entries 3 and 12). However, a reverse trend was observed for palladium benzamidine complexes with pendant pyridine functionality (entries 5 and 13).



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Scheme 3. The palladacycles bearing the benzamidinate ligand precursor.[8]

Conclusion

One new benzamidinate ligand precursor and four palladium complexes were prepared and fully characterized. The catalytic activity of two palladacycles for the Suzuki reaction has been demonstrated. On the basis of the molecular structures of palladium chelates and palladacyclic complexes, thet formation of six-membered palladacycles actually proceeds through a palladium chelate complex as an intermediate followed by a C–H activation process, which was proposed in our previous report. Once the *ortho* position for the formation of a six-membered palladacycle had been blocked, the C–H activation process could take place on the other *ortho* position to form a five-membered palladacycle slowly. On the basis of those results demonstrated by palladium benzamidinate complexes, formation of the six-membered palladacycle seems to be faster than that of the five-membered palladacycle. Under optimized conditions, **3** exhibits catalytic activity with lower catalyst loading (10^{-5} to 10^{-7}) and with electronically deactivated aryl bromide in the Suzuki reaction. Complex **3** also demonstrates catalytic activity with a less reactive aryl chloride-containing electron-withdrawing group.

Experimental Section

General: All manipulations were carried out under an atmosphere of dinitrogen by using standard Schlenk line or drybox techniques. Solvents were heated at reflux over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried with molecular sieves.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded either with Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in [D]chloroform at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed with an Elementar Vario ELIV instrument.

$Pd(OAc)_2$ (Aldrich), 2,6-diisopropylaniline (Alfa), 2-(aminomethyl)pyridine (Acros) and *N*,*N*-dimethylethyleneamine (Acros) were used as supplied. NEt_3 was dried with CaH_2 and distilled before use. *N*-(2,6-Diisopropylphenyl)benzanilide and *N*-(2,6-diisopropylphenyl)benzimidoyl chloride were prepared according to modified literature procedures.[9a]

Preparations

{Ph–C[=N–(2,6-di-*i*Pr–C_6H_3)][$NH(CH_2)_2NMe_2$]}: A solution of *N*-(2,6-diisopropylphenyl)benzimidoyl chloride (0.9 g, 3 mmol) and NEt_3 (0.70 mL, 4.6 mmol) in toluene (15 mL) was treated with *N*,*N*-dimethylethyleneamine (0.35 mL, 3.4 mmol) at 0 °C then allowed to warm to room temperature. After 24 h of stirring, the volatile compounds were removed under reduced pressure and the residue was extracted with hexane (50 mL). The extract was pumped to dryness to afford a yellow oily product; yield 0.65 g, 62%. This compound has been reported in the literature.[9b,9c]

{Ph–C[=N–(2,6-di-*i*Pr–C_6H_3)]($NHCH_2Py$)}: The preparation of {Ph–C[=N–(2,6-di-*i*Pr–C_6H_3)]($NHCH_2Py$)} was similar to that used for {Ph–C[=N–(2,6-di-*i*Pr–C_6H_3)][$NH(CH_2)_2NMe_2$]} but with *N*-(2,6-diisoproyplphenyl)benzimidoyl chloride (1.5 g, 5 mmol), NEt_3 (0.84 mL, 6 mmol) and 2-(aminomethyl)pyridine (0.52 mL, 5 mmol). The volatile compounds were removed under reduced pressure and the residue was extracted with toluene (50 mL). The extract was pumped to dryness to afford an orange solid; yield 1.62 g, 87.4%. ^1H NMR (600 MHz, 333 K): δ = 0.97 [s, 6 H, *i*Pr–$(CH_3)_2$], 1.10 [s, 6 H, *i*Pr–$(CH_3)_2$], 3.03 (s, 2 H, *i*Pr–*H*), 4.64 (s, 2 H, CH_2Py), 5.64 (s, 1 H, N*H*), 6.91 (s, 1 H), 6.97 (s, 2 H), 7.13 (m, 1 H), 7.26 (br., 4 H), 7.38 (br., 2 H), 7.60 (t, J = 7.2 Hz, 1 H), 8.51 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, 333 K): δ = 22.6 (s, CH_3–*i*Pr), 23.7 (s, CH_3–*i*Pr), 28.2 (s, *C*H–*i*Pr), 47.9 (s, *C*H–Py), 122.0, 122.3, 122.8, 127.9, 128.2, 129.2, 136.3, 149.2 (*C*H–Ph and *C*H–Py), 135.7, 138.7, 145.1, 154.4, 158.3 (C_{ipso}–C_6H_5, C_{ipso}–Py and one

*C*NN) ppm. $C_{25}H_{29}N_3$ (371.52): calcd. C 80.82, H 7.87, N 11.31; found C 80.74, H 7.53, N 11.27.

Complex 1: CH_2Cl_2 (15 mL) was added at room temperature to a flask that contained {Ph–C[=N–(2,6-di-*i*Pr–C_6H_3)][NH(CH_2)$_2$-NMe_2]} (0.35 g, 1 mmol) and $Pd(OAc)_2$(0.22 g, 1 mmol). After 1 h of stirring, the volatile compounds were removed under reduced pressure to afford a brown solid. The resulting solid was purified by THF/hexane solution to afford a pale yellow solid; yield 0.44 g, 76%. ^{1}H NMR (600 MHz): δ = 1.12 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 1.18 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 1.82 [s, 3 H, O–C(=O)CH_3], 1.99 [s, 3 H, O–C(=O)CH_3], 2.34 (t, J = 6.0 Hz, 2 H, CH_2), 2.71 [s, 6 H, N(CH_3)$_2$], 3.07 (t, J = 6.0 Hz, 2 H, CH_2), 3.24 [sept, J = 6.6 Hz, 2 H, CH–(CH_3)$_2$], 6.91 (d, J = 7.8 Hz, 2 H, CH–Ar), 6.94 (m, 2 H, CH–Ar), 7.07 (t, J = 7.2 Hz, 1 H, CH–Ar), 7.19–7.26 (m, 3 H, CH–Ar), 9.99 (s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.7 [s, CH–(CH_3)$_2$], 23.5 [s, O–C(=O)CH_3], 23.6 [s, O–C(=O)CH_3], 25.6 [s, CH–(CH_3)$_2$], 28.6 [s, CH–(CH_3)$_2$], 50.7 [s, N(CH_3)$_2$], 53.0 (s, CH_2), 65.8 (s, CH_2), 123.0, 127.0, 128.3, 128.4, 130.1 (*C*H–Ar), 129.9, 131.8, 146.6, 168.6 [two C_{ipso}–Ar, one *C*NN and one *C*–CH–(CH_3)$_2$], 178.1 [s, O–*C*(=O)CH_3] ppm. $C_{27}H_{39}N_3O_4Pd$ (576.02): calcd. C 56.30, H 6.82, N 7.29; found C 56.36, H 6.71, N 7.25.

Complex 2: The procedure for preparation of **2** was similar to that used for **1** but with {Ph–C(NHCH$_2$Py)[=NH–(2,6-di-*i*Pr–C_6H_3)]} (0.37 g, 1 mmol) and $Pd(OAc)_2$ (0.25 g, 1.1 mmol). A yellow solid was obtained; yield 0.57 g, 96%. ^{1}H NMR (600 MHz): δ = 1.10 [d, J = 7.2 Hz, 6 H, CH–(CH_3)$_2$], 1.20 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 1.91 [s, 3 H, O–C(=O)CH_3], 2.09 [s, 3 H, O–C(=O)CH_3], 3.25 [sept, J = 6.6 Hz, 2 H, CH–(CH_3)$_2$], 4.53 (s, 2 H, CH_2Py), 6.93 (d, J = 7.8 Hz, 2 H, CH–Ar), 7.00 (m, 2 H, CH–Ar), 7.06–7.10 (overlap, 2 H, CH–Ar), 7.25–7.32 (overlap, 4 H, CH–Ar), 7.78 (m, 1 H, CH–Ar), 8.19 (d, J = 6 Hz, 1 H, CH–Ar), 10.20 (s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.6 [s, CH–(CH_3)$_2$], 23.4 [s, O–C(=O)CH_3], 25.6 [s, CH–(CH_3)$_2$], 28.5 [s, CH–(CH_3)$_2$], 62.6 (s, CH_2Py), 119.6, 123.06, 123.12, 127.1, 128.46, 128.54, 130.4, 138.8, 148.9 (*C*H–Ar), 129.1, 131.5, 146.6, 162.1, 168.9 [three C_{ipso}–Ar, one N*C*N and one *C*–CH–(CH_3)$_2$], 178.2, 178.9 [O–*C*(=O)CH_3] ppm. $C_{27}H_{39}N_3O_4Pd$ (576.02): calcd. C 58.44, H 5.92, N 7.05; found C 58.59, H 5.49, N 6.99.

Complex 3: A solution of **1** (0.58 g, 1 mmol) in toluene (15 mL) was heated at 80 °C for 48 h. The volatile compounds were removed under reduced pressure and the residue was purified by THF/hexane solution to obtain a white precipitate. The crude product was washed hexane (30 mL three times) to afford white solid; yield 0.46 g, 90%. ^{1}H NMR (600 MHz): δ = 1.16 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 1.27 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 2.11 [s, 3 H, O–C(=O)CH_3], 2.56 [overlap, 8 H, CH_2 and N(CH_3)$_2$], 2.84 (br., 2 H, CH_2), 3.21 [sept, J = 6.6 Hz, 2 H, CH–(CH_3)$_2$], 6.67 (br., 1 H, NH), 6.80 (br., 1 H, CH–Ar), 6.96 (br., 1 H, CH–Ar), 7.12 (t, J = 7.2 Hz, 1 H, CH–Ar), 7.20 (d, J = 7.8 Hz, 2 H, CH–Ar), 7.21 (t, J = 8.4 Hz, 1 H, CH–Ar), 7.38 (t, J = 7.8 Hz, 1 H, CH–Ar) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 22.6 [s, CH–(CH_3)$_2$], 24.15 [s, O–C(=O)CH_3], 24.24 [s, CH–(CH_3)$_2$], 28.6 [s, CH–(CH_3)$_2$], 46.6 (s, CH_2), 47.4 [s, N(CH_3)$_2$], 63.6 (s, CH_2), 123.3, 123.8, 129.4, 130.4, 133.9 (*C*H–Ar), 122.7, 132.2, 144.9, 146.8, 152.5, 161.8 [two C_{ipso}–Ar, one N*C*N, two *C*–CH–(CH_3)$_2$ and one metalated *C*–Ph], 177.5 [s, O–*C*(=O)CH_3] ppm. $C_{25}H_{35}N_3O_2Pd$ (515.97): calcd. C 58.19, H 6.84, N 8.14; found C 57.69, H 6.25, N 8.04.

Complex 4: A solution of **2** (0.57 g, 0.96 mmol) in THF (3 mL) was heated at 80 °C for 3 h. The brown suspension was cooled to room temperature and filtered. The brown residue was washed with THF to afford a pale grey solid; yield 0.57 g, 59%. ^{1}H NMR (600 MHz): δ = 1.14 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 1.26 [d, J = 6.6 Hz, 6 H, CH–(CH_3)$_2$], 2.21 [s, 3 H, O–C(=O)CH_3], 3.25 [sept, J = 6.6 Hz, 2 H, CH–(CH_3)$_2$], 4.52 (br., 2 H, CH_2Py), 6.83 (s, 1 H, NH), 6.87 (br., 1 H, CH–Ar), 7.12 (br., 1 H, CH–Ar), 7.17 (m, 2 H, CH–Ar), 7.24 (m, 3 H, CH–Ar), 7.42 (t, J = 7.8 Hz, 1 H, CH–Ar), 7.59 (t, J = 7.2 Hz, 1 H, CH–Ar), 8.35 (d, J = 5.4 Hz, 1 H, CH–Ar) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 22.9 [br., CH–(CH_3)$_2$], 24.1 [br., CH–(CH_3)$_2$], 24.4 [s, O–C(=O)CH_3], 28.6 [s, CH–(CH_3)$_2$], 55.7 (s, CH_2–Py), 120.9, 122.7, 123.2, 123.9, 124.4, 129.5, 130.7, 133.7, 137.8, 149.0 (*C*H–Ar), 132.0, 145.1, 147.0, 148.8, 152.9, 162.0 [three C_{ipso}–Ar, one metalated *C*–Ph, one *C*–CH–(CH_3)$_2$ and one N*C*N], 177.8 [s, O–*C*(=O)CH_3] ppm. $C_{27}H_{39}N_3O_4Pd$ (576.02): calcd. C 60.50, H 5.83, N 7.84; found C 60.55, H 6.19, N 7.37.

General Procedure for the Suzuki-Type Coupling Reaction: Prescribed amounts of catalyst, aryl halide (1.0 equiv.), phenylboronic acid (1.5 equiv.), base (3.0 equiv.) and a magnetic stir bar were placed in a Schlenk tube under nitrogen. Toluene (3 mL) was added by syringe, and the reaction mixture was heated in an oil bath at the prescribed temperature for the prescribed time. After removal of the volatile compounds, the residue was diluted with ethyl acetate, then filtered through a pad of silica gel. A sample in [D]chloroform was taken for determination of conversion. The crude material was further purified by flash chromatography on silica gel.

Crystal Structure Data: The crystals were grown from a solution of **1** in dichloromethane/hexane or a solution of **4** in concentrated chloroform, then isolated by filtration. Suitable crystals of **1** were sealed in thin-walled glass capillaries under a nitrogen atmosphere at 293 K and mounted on a Bruker AXS SMART 1000 diffractometer. A crystal of **4** was mounted onto a glass fibre by using a perfluoropolyether oil "oil-drop" method and cooled rapidly in a stream of cold nitrogen gas with an Oxford Cryosystems Cryostream unit. Diffraction data were collected at 100 K with an Oxford Gemini S diffractometer. The absorption correction was carried out on the basis of symmetry-equivalent reflections by using SADABS for **1**, and semiempirical absorption correction was based on the spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm from Crysalis RED, Oxford Diffraction Ltd for **4**.[14]

Table 2. Summary of crystal data for compounds **1** and **4**.

	1·CH_2Cl_2	**4**·$CHCl_3$·H_2O
Formula	$C_{28}H_{39}Cl_2N_3O_4Pd$	$C_{28}H_{34}Cl_3N_3O_3Pd$
M_r	658.92	673.33
T [K]	297(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	10.3443(14)	9.9600(3)
b [Å]	22.158(3)	18.5872(5)
c [Å]	14.4909(18)	16.5409(5)
α [°]	90	90
β [°]	107.768(2)	101.862(2)
γ [°]	90	90
V [Å^3]	3163.0(7)	2996.80(15)
Z	4	4
$\rho_{calcd.}$ [Mgm^{-3}]	1.384	1.492
μ(Mo-K_α) [mm^{-1}]	0.791	0.920
Reflections collected	17578	28387
Parameters	356	363
Indep. reflections (R_{int})	6182 (0.0269)	7152 (0.0385)
Final R indices R_1[a], wR_2[a]	0.0408, 0.1139	0.0356, 0.0889
R indices (all data)	0.0517, 0.1215	0.0505, 0.0927
GoF[b]	1.041	1.019

[a] $R_1 = [(\Sigma|F_o| - |F_c|)/\Sigma|F_o|]$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, w = 0.10. [b] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

The space-group determination was based on a check of the Laue symmetry and systematic absences and was confirmed by using the structure solution. The structure was solved by direct methods using a SHELXTL package.[15] All non-hydrogen atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms, and fixed isotropic parameters were used for hydrogen atoms. Some details of the data collection and refinement are given in Table 2.

CCDC-840682 (for **1**) and -840683 (for **4**) 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.

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