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Palladacycles bearing pendant benzamidinate ligands as catalysts for the Suzuki and Heck coupling reactions

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Abstract—Three pendant benzamidines [Ph–C(=NC_6H_5)–{$NH(CH_2)_2NMe_2$}] (**1**), [Ph–C(=NC_6H_5)–{$NH(CH_2Py)$}] (**2**) and [Ph–C(=NC_6H_5)-{$NH(o\text{-}C_6H_4)$(oxazoline)}] (**3**) are described. Reactions of **1**, **2** or **3** with one molar equivalent of $Pd(OAc)_2$ in THF give the palladacyclic complexes [Ph–C{–$NH(\eta^1\text{-}C_6H_4)$}{=$N(CH_2)_2NMe_2$}]Pd(OAc) (**4**), [Ph–C{–$NH(\eta^1\text{-}C_6H_4)$}{=N (CH_2Py)}]Pd(OAc) (**5**) and [Ph–C{–$NH(\eta^1\text{-}C_6H_4)$}{=$N(o\text{-}C_6H_4)$(oxazoline)}]Pd(OAc) (**6**), respectively. Treatment of **4**, **5** or **6** with excess of LiCl in chloroform affords [Ph–C{–$NH(\eta^1\text{-}C_6H_4)$}{=$N(CH_2)_2NMe_2$}]PdCl (**7**), [Ph–C{–$NH(\eta^1\text{-}C_6H_4)$}{=$N(CH_2Py)$}]PdCl (**8**) and [Ph–C{–$NH(\eta^1\text{-}C_6H_4)$}{=$N(o\text{-}C_6H_4)$(oxazoline)}]PdCl (**9**). The crystal and molecular structures are reported for compounds **1**, **3**, **5**, **6** and **7**. The application of these palladacyclic complexes to the Suzuki and Heck coupling reactions was examined.

1. Introduction

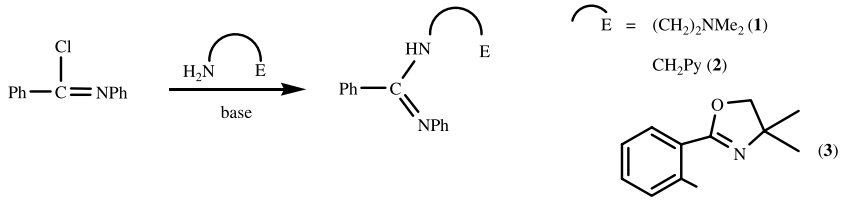
Amidinates of the general formula $[R^1C(NR^2)(NR^3)]^{-1}$, have been the focus of attention because they can often be employed extensively in main group and transition-metal coordination chemistry, organometallic chemistry and catalysis.[1–4] Over the past decades, a large diversity of metal–amidinato compounds has been synthesised and these have been reviewed by Barker and Kilner (on amidine) and Edelmann (on benzamidine).[1,2] Due to the steric and electronic properties of amidinato ligands, they can be easily substituted by variation of the substituents on either or both N and C atoms. Recently several types of amidinato ligands with pendant functionality were explored to act as three-coordinate, six-electron-donor ligands.[5–11] In some cases, the existence of pendant arm could play an important role in determining the constitution of the resulting complexes[6–10] or affecting the reactivity of metal complexes in catalytic reactions.[5] Palladium amidinato compounds have been studied for several decades.[12–18] However, palladium complexes supported by pendant benzamidinato ligands, on our knowledge, have not been reported.

In this paper, we report the preparation and structural properties of pendant benzamidines and their orthometallated palladium complexes. The catalytic activities of these palladacyclic complexes toward the Suzuki and Heck coupling reactions are investigated.

2. Results and discussion

2.1. Preparations of ligand precursors and palladacycles

Preparation of the desired amidines follows a classical route for the synthesis of *N*,*N*′-disubstituted amidines.[19]



Scheme 1.

Keywords: Pendant benzamidine; Palladacyclic complexes; Oxazoline; Suzuki reaction; Heck reaction.
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Treatment of the *N*-(phenyl)benzimidoyl chloride with 1 mol equiv of amines or substituted aniline in the presence of triethylamine affords amidines **1**, **2** and **3** in moderate yield, as shown in Scheme 1. Compounds are characterised by NMR spectroscopy as well as elemental analyses. Crystals suitable for X-ray refinement were grown from concentrated hexane (for **1**) or toluene/hexane (for **3**) solution. The crystal structures of amidines **1** and **3** have been determined and the molecular structures are shown in Figures 1 and 2. Selected bond lengths and angles are listed in Tables 1 and 2. The two C–N bonds in each amidine (1.293(3) and 1.348(3) Å for **1**; 1.269(2), 1.282(3) and 1.381(2), 1.384(3) Å for **3**) are similar in length to those reported for other benzamidines[19–21] and pendant amidine,[6,22,23] indicating the localized property of the imine C=N and amine C–N bonds. The bond angles around imino C and N atoms in each amidine are around 120°, indicating the nature of sp^2 centres.

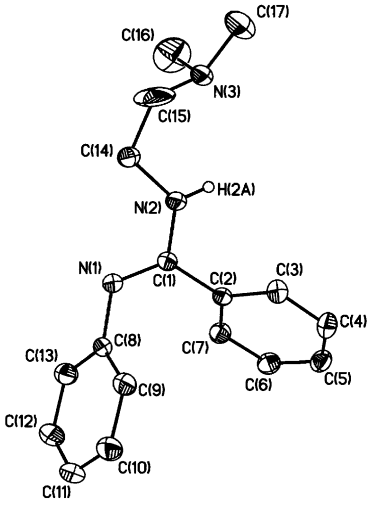


Figure 1. Molecular structure of compound **1**. Hydrogen atoms on carbon atoms omitted for clarity.

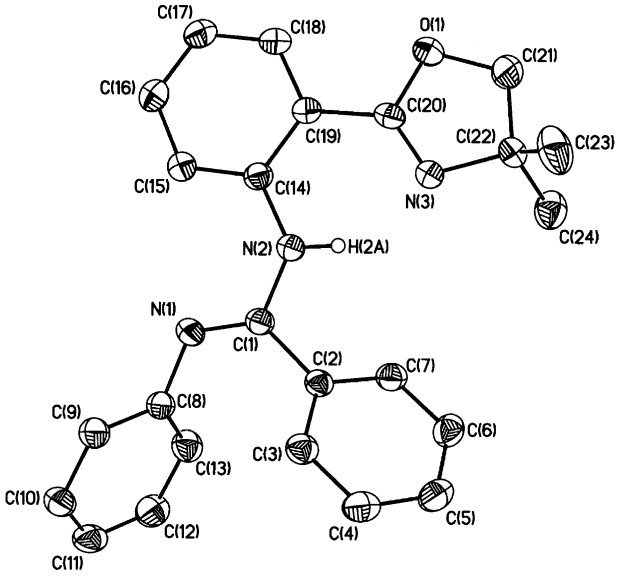


Figure 2. Molecular structure of one of the crystallographically independent molecules of complex **3**. Hydrogen atoms on carbon atoms omitted for clarity.

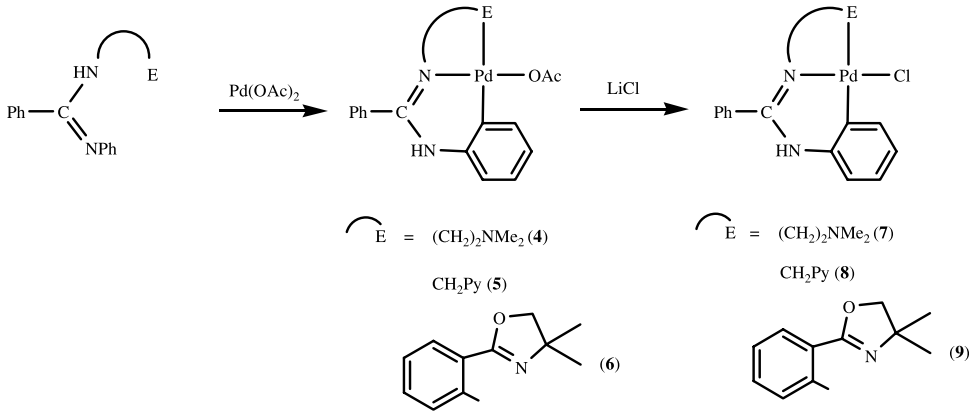
Table 1. Selected bond lengths (Å) and angles (°) for **1**

N(1)–C(1)	1.293(3)	N(2)–C(1)	1.348(3)
N(1)–C(8)	1.415(3)	N(2)–C(14)	1.433(4)
C(1)–C(2)	1.492(4)		
C(1)–N(1)–C(8)	121.0(2)	C(1)–N(2)–C(14)	124.4(3)
N(1)–C(1)–N(2)	119.0(2)	N(1)–C(1)–C(2)	125.8(2)
N(2)–C(1)–C(2)	115.2(2)		

Table 2. Selected bond lengths (Å) and angles (°) for **3**

N(1)–C(1)	1.269(2)	N(2)–C(1)	1.381(2)
N(1)–C(8)	1.409(3)	N(2)–C(14)	1.388(2)
C(1)–C(2)	1.497(3)	C(25)–C(26)	1.486(3)
N(4)–C(25)	1.282(3)	N(5)–C(25)	1.384(3)
N(4)–C(32)	1.408(3)	N(5)–C(38)	1.390(3)
C(1)–N(1)–C(8)	122.33(19)	C(1)–N(2)–C(14)	130.40(18)
N(1)–C(1)–N(2)	121.33(19)	N(1)–C(1)–C(2)	127.49(19)
N(2)–C(1)–C(2)	111.07(18)	N(5)–C(25)–C(26)	112.7(2)
C(25)–N(4)–C(32)	123.59(19)	C(25)–N(5)–C(38)	131.2(2)
N(4)–C(25)–N(5)	120.3(2)	N(4)–C(25)–C(26)	127.0(2)

Three pendant amidines react readily with 1 mol equiv of $Pd(OAc)_2$ in dichloromethane to afford complexes **4**, **5** and **6**, which are expected to form a mononuclear species[22] rather than the dimeric or oligomeric structures.[15–17] A summary of the syntheses and proposed structures of palladacycles is shown in Scheme 2. In each palladium acetate compound, one N*H* singlet around δ 9–10 ppm (9.71 ppm for **4**; 9.64 ppm for **5**; 10.10 ppm for **6**) was found on the ^{1}H NMR spectrum and one more tertiary carbon appeared in the region of phenyl ring on the $^{13}C\{^1H\}$ NMR spectrum, which indicate the preference of carbon metallation rather than the N*H* deprotonation.[16] Suitable crystals of **5** for structural determination were obtained from concentrated CH_2Cl_2 solution. The molecular structure is shown in Figure 3 and selected bond lengths and angles are listed in Table 3. The structural analysis showed the target complex as a mononuclear species. The bond angles (from 81.37(11) to 93.82(12)°) around Pd metal centre indicate a complex having a slightly distorted square planar geometry, in which the palladium metal centre is coordinated with one pyridine nitrogen atom, one imine nitrogen atom, one metallated carbon atom, and one acetate oxygen atom to form one five-membered metallacycle and one six-membered metallacycle. The bond lengths of Pd–N_{py} (2.119(3) Å) and Pd–$C_{metallated}$ (1.975(4) Å) are within those (1.964(3)–2.150(3) Å for Pd–N_{py}; 1.961(4)–2.019(2) Å for Pd–$C_{metallated}$) found in metallated palladacycles.[16,24–29] The bond length of Pd–O_{OAc} (2.064(3) Å) is among those (2.032(2)–2.126(3) Å) found in palladacycles.[28–31] The bond length of Pd–$N_{C=N}$ (1.981(3) Å) is close to those (1.969(6)–2.071(3) Å) found in palladacycles.[16,29,32–34] The C–N bond lengths of NCN moiety are not equal with 1.343(4) and 1.309(4) Å, respectively, indicating the localized nature of the imine C=N and amine C–N bonds. Suitable crystals of **6** for structural determination are obtained from CH_2Cl_2/hexane solution. The molecular structure is shown in Figure 4, and selected bond lengths and angles are listed in Table 4. Basically, compound **6** is quite similar to compound **5** with different pendant group C_6H_4Oxazoline instead of CH_2Py for **5**. The palladium metal centre is coordinated with similar coordination types as in **5** except one nitrogen atom from oxazoline instead of one pyridine nitrogen atom to form two six-membered



Scheme 2.

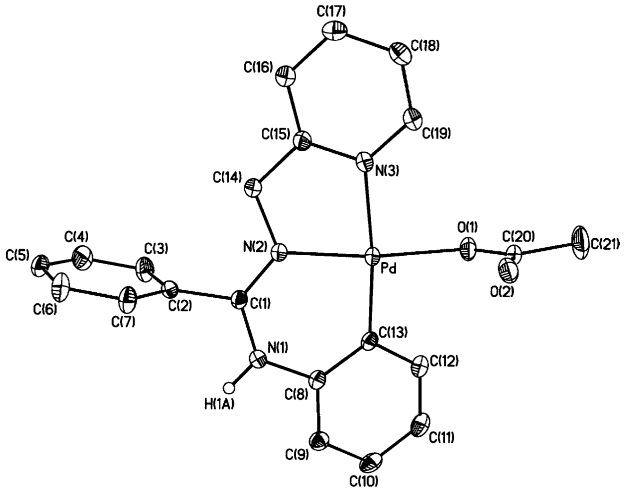


Figure 3. Molecular structure of complex **5**. Hydrogen atoms on carbon atoms omitted for clarity.

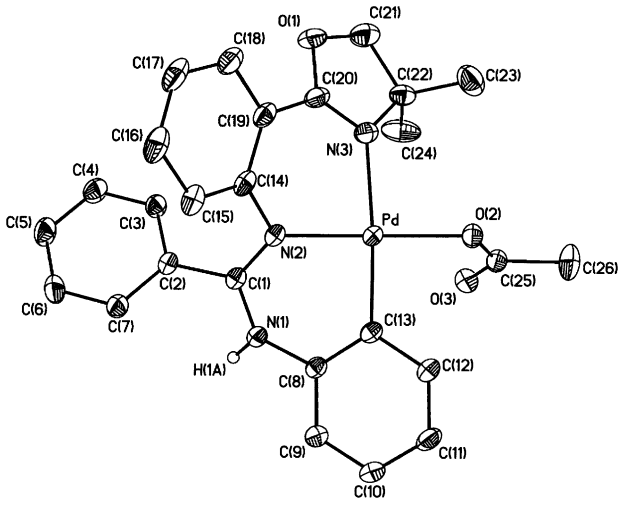


Figure 4. Molecular structure of complex **6**. Hydrogen atoms on carbon atoms omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **5**

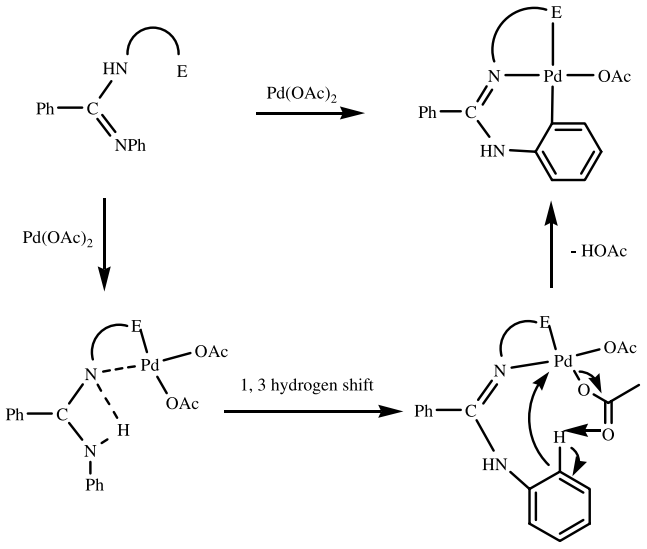
Pd–C(13)	1.975(4)	Pd–N(2)	1.981(3)
Pd–N(3)	2.119(3)	Pd–O(1)	2.064(3)
N(1)–C(1)	1.343(4)	N(1)–C(8)	1.416(4)
N(2)–C(1)	1.309(4)	N(2)–C(14)	1.462(4)
N(2)–Pd–C(13)	92.31(13)	N(2)–Pd–N(3)	81.37(11)
C(13)–Pd–O(1)	92.68(13)	N(3)–Pd–O(1)	93.82(12)
C(13)–Pd–N(3)	173.32(12)	N(2)–Pd–O(1)	172.33(11)

Table 4. Selected bond lengths (Å) and angles (°) for **6**

Pd–C(13)	1.979(3)	Pd–N(2)	2.007(3)
Pd–N(3)	2.144(3)	Pd–O(2)	2.045(2)
N(1)–C(1)	1.334(4)	N(1)–C(8)	1.428(4)
N(2)–C(1)	1.308(4)	N(2)–C(14)	1.427(4)
N(2)–Pd–C(13)	88.35(13)	N(2)–Pd–N(3)	87.77(13)
C(13)–Pd–O(2)	91.30(13)	N(3)–Pd–O(2)	92.85(12)
C(13)–Pd–N(3)	174.55(13)	N(2)–Pd,O(2)	175.73(11)

metallacycles. Bond lengths and bond angles are similar to those discussed above. Due to the rigidity of the pendant arm, the bond length of Pd–$N_{oxazoline}$ (2.144(3) Å) is a bit longer than those (1.97(2)–2.060(10) Å) found in metallated palladacycles.[35–38] Similar to compound **5**, the C–N bond lengths of NCN moiety in **6** are not equal (1.334(4) Å for C(1)–N(1) and 1.308(4) Å for C(1)–N(2)). Compare with the bond lengths (1.269(2) Å for C(1)–N(1) and 1.282(3) Å for C(25)–N(4); 1.381(2) Å for C(1)–N(2) and 1.384(3) Å for C(25)–N(5)) in **3**, a 1,3 hydrogen shift process might happen in the formation of compounds **4**–**6**. Plausible mechanism for the formation of palladium acetate complexes is proposed in Scheme 3. Possible reaction is the coordination of benzamidine to the palladium metal centre, followed by the shift of proton from the nitrogen atom on the amine group to the nitrogen atom on the imine group,[29] which is induced by the metal centre. The orthometallation is then achieved by removal of 1 equiv of HOAc to form the target compound.[28] This phenomenon could not be observed in the synthesis of palladacycles bearing amidinato ligands with symmetrical substituents on both nitrogen atoms.[16]

Complexes **7**–**9** were synthesised by the reaction of palladium acetate compounds **4**–**6** with excess lithium chloride in chloroform at room temperature. The NMR spectroscopic data and elemental analysis of each compound are indicative of cyclometallated complex with a Cl atom instead of an acetate group in those palladium acetate compounds. Suitable crystals of **7** for structural determination were obtained from CH_2Cl_2/hexane solution. The molecular structure is shown in Figure 5, and selected bond



Scheme 3.

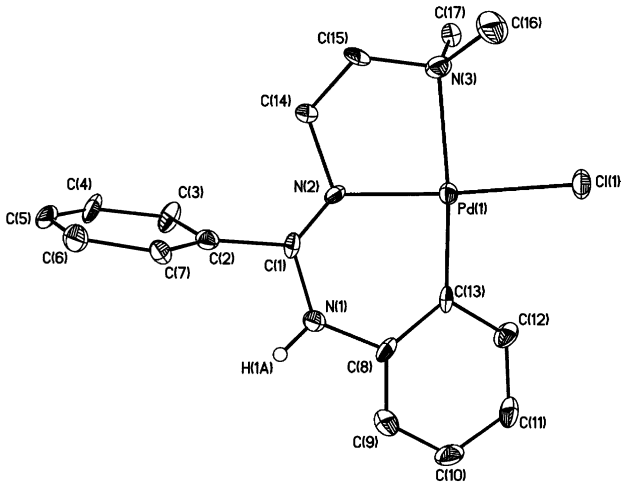


Figure 5. Molecular structure of one of the crystallographically independent molecules of complex **7**. Hydrogen atoms on carbon atoms omitted for clarity.

lengths and angles are listed in Table 5. Basically, compound **7** is similar to compound **5** with different pendant group $CH_2CH_2NMe_2$ instead of CH_2Py for **5**. The palladium metal centre is coordinated with one amine nitrogen atom, one imine nitrogen atom, one metallated carbon atom and one chloride atom to form one five-membered metallacycle and one six-membered metallacycle. Bond lengths and bond angles are similar to those discussed above. The bond lengths of Pd–N_{amine} (2.207(10) and 2.171(11) Å) is close to those (2.069(6)–2.203(3) Å) found in metallated palladacycles.[29–33,39–43] The bond lengths of Pd–Cl (2.328(4) and 2.331(4) Å) is close to those (2.304(2)–2.377(1) Å) found in metallated palladacycles.[25,27,29,32–34]

Table 5. Selected bond lengths (Å) and angles (°) for **7**

Pd(1)–C(13)	1.922(13)	Pd(1)–N(2)	2.002(10)
Pd(1)–N(3)	2.207(10)	Pd(1)–Cl(1)	2.328(4)
N(1)–C(1)	1.398(15)	N(1)–C(8)	1.426(18)
N(2)–C(1)	1.171(15)	N(2)–C(14)	1.490(15)
Pd(2)–C(30)	2.033(12)	Pd(2)–N(5)	1.984(9)
Pd(2)–N(6)	2.171(11)	Pd(2)–Cl(2)	2.331(4)
N(4)–C(18)	1.302(14)	N(4)–C(25)	1.395(17)
N(5)–C(18)	1.439(14)	N(5)–C(31)	1.439(15)
N(2)–Pd(1)–C(13)	89.3(4)	N(2)–Pd(1)–N(3)	85.0(4)
C(13)–Pd(1)–Cl(1)	94.5(3)	N(3)–Pd(1)–Cl(1)	91.1(3)
C(13)–Pd(1)–N(3)	174.2(5)	N(2)–Pd(1)–Cl(1)	176.0(3)
N(5)–Pd(2)–C(30)	92.9(5)	N(5)–Pd(2)–N(6)	81.9(4)
C(30)–Pd(2)–Cl(2)	95.1(4)	N(6)–Pd(2)–Cl(2)	90.1(3)
C(30)–Pd(2)–N(6)	174.7(5)	N(5)–Pd(2)–Cl(2)	172.0(3)

2.2. Suzuki-type reaction using CNN-type palladacycles

Since several palladacycles containing CNN-type ligands can be used as catalysts for the carbon–carbon coupling reactions,[29,45,46] the palladacyclic derivatives **4–9** were expected to work as catalysts toward the Suzuki-type coupling reaction. In order to examine the catalytic activity, optimised conditions using the coupling of 4-bromoacetophenone with 1.5 equiv phenylboronic acid catalysed by 1 mol% **4–9** in the presence of 3 equiv base at 80 °C were conducted. The rate of the Suzuki-type reaction is solvent-dependent with trials on *N*,*N*-dimethylacetamide (DMA), THF, and toluene. For the best choice of a base, we surveyed K_3PO_4, Cs_2CO_3, and KF. Selected results are listed in Table 6. Finally, we found that use of KF for **4** and **7** and K_3PO_4 for **5**, **6**, **8** and **9** in toluene leads to the best conversion within 1 h (entries 1–6). Excellent conversion is observed with 1 mol% **6** using 4-bromobenzaldehyde under the same condition (entry 7). Similar conditions were applied to examine the catalytic activities of **4–9** using 4-bromoanisole as substrate. Comparable conversions were observed within 3 h (entries 8–13). Similar conversions were observed with 1 mol% **6** using various substrates with electron-donating substituents under the optimised condition (entries 14–15). Due to the better activity and solubility of **6**, lower catalyst concentrations were investigated with **6** using catalyst/substrate ratios from 10^{-3} to 5×10^{-5}. The reactions gave degrees of conversion to 99% within 2 h for 10^{-3} ratio, 93% within 5 h for 10^{-4} ratio, and 80% within 8 h for 5×10^{-5} ratio (entries 16–18). The coupling reactions were also carried out with 1 mol% **6** using less reactive substrates under the optimised conditions. As expected, the degrees of conversion became lower with longer period of time (entries 19–21).

2.3. Heck reaction using CNN-type palladacycles

We also examined the catalytic activities of **6** in Heck reaction using the coupling of 4-bromoacetophenone with styrene. Selected results are listed in Table 7. Optimised conditions, Cs_2CO_3/toluene and Cs_2CO_3/DMA under refluxing temperatures, seem to be the best choices after several trials on the combinations of solvents and bases (entries 1–3). Similar conversions were observed using various substrates with electronically activated substituents under the optimised condition (entries 4–5). Coupling reactions were also carried out with 1 mol% **6** and Cs_2CO_3/toluene under refluxing temperature using substrates with electronically deactivated substituents. As expected, over 90% conversions were observed within longer period of time (entries 6–8). The optimised condition, Cs_2CO_3/DMA under refluxing temperature, seems not suitable for substrate with electronically deactivated substituent. Poor conversion was observed

Table 6. Suzuki-type coupling reaction catalysed by new palladium complexes[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol%)	*t* (h)	Conversion (%)[b]	Yield (%)[c]
1	**4**	4-Bromoacetophenone	KF	Toluene	1	1	78	70
2	**5**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	86	79
3	**6**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	99	91
4	**7**	4-Bromoacetophenone	KF	Toluene	1	1	81	74
5	**8**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	86	78
6	**9**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	98	91
7	**6**	4-Bromobenzaldehyde	K_3PO_4	Toluene	1	1	99	93
8	**4**	4-Bromoanisole	KF	Toluene	1	3	72	65
9	**5**	4-Bromoanisole	K_3PO_4	Toluene	1	3	84	75
10	**6**	4-Bromoanisole	K_3PO_4	Toluene	1	3	91	84
11	**7**	4-Bromoanisole	KF	Toluene	1	3	71	63
12	**8**	4-Bromoanisole	K_3PO_4	Toluene	1	3	79	73
13	**9**	4-Bromoanisole	K_3PO_4	Toluene	1	3	90	84
14	**6**	4-Bromotoluene	K_3PO_4	Toluene	1	3	98	92
15	**6**	1-Bromo-4-*tert*-butyl-benzene	K_3PO_4	Toluene	1	3	93	88
16	**6**	4-Bromoacetophenone	K_3PO_4	Toluene	0.1	2	99	92
17	**6**	4-Bromoacetophenone	K_3PO_4	Toluene	0.01	5	93	86
18	**6**	4-Bromoacetophenone	K_3PO_4	Toluene	0.005	8	80	74
19	**6**	4-Chloroacetophenone	K_3PO_4	Toluene	1	18	73	65
20	**6**	4-Chloro-benzoic acid methylester	K_3PO_4	Toluene	1	18	66	60
21	**6**	4-Chloroanisole	K_3PO_4	Toluene	1	24	20	–

[a] Reaction conditions: 1 mmol aryl halide, 1.5 mmol phenylboronic acid, 3.0 mmol base, 3 ml solvent, 80 °C.
[b] Determined by ^{1}H NMR.
[c] Isolated yield. (average of two experiments).

within the same period of time (entry 9). Lower catalyst concentrations were investigated with both optimised conditions using catalyst/substrate ratios from 10^{-3} to 10^{-4}. Better conversions were observed using high temperature conditions (entries 10–13). Compound **6** also showed catalytic activities in catalysing the less reactive substrates, such as 4-chloroacetophenone. Higher conversion was observed using Cs_2CO_3/DMA under refluxing temperature as reaction condition (entries 14–15). Better conversion was observed using 2 mol% catalyst loadings within 24 h (entry 16).

3. Summary

We have demonstrated the preparations and catalytic studies towards the Suzuki and Heck coupling reactions of mononuclear palladacycles supported by pendant benzamidinate ligands. Based on the structural analysis, a 1,3 hydrogen shift process might happen upon the formation of six-membered metallacycle, which could not be observed in the synthesis of palladacycles bearing amidinato ligands with symmetrical substituents on both nitrogen atoms. Plausible mechanism for the formation of the palladacycles has been proposed. The catalytic data show that palladacyclic complexes bearing pendant oxazoline group exhibit better activities than those with pendant pyridine or amine groups. Under optimised conditions, **6** exhibits catalytic efficiency with lower catalyst loadings, and with less reactive substrates in both Suzuki and Heck coupling reactions. Preliminary studies on the modification of benzamidines with different substituents and their application in the synthesis of metal complexes are currently being undertaken.

Table 7. Heck coupling reaction catalysed by new palladium complexes[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol%)	*T* (°C)	*t* (h)	Conversion (%)[b]	Yield (%)[c]
1	**6**	4-Bromoacetophenone	Cs_2CO_3	Toluene	1	110	2	95	90
2	**6**	4-Bromoacetophenone	Cs_2CO_3	DMA	1	135	2	99	93
3	**6**	4-Bromoacetophenone	KF	DMA	1	135	2	90	85
4	**6**	Methyl 4-bromobenzoate	Cs_2CO_3	Toluene	1	110	2	90	85
5	**6**	4-Bromobenzaldehyde	Cs_2CO_3	Toluene	1	110	2	92	83
6	**6**	4-Bromoanisole	Cs_2CO_3	Toluene	1	110	8	94	88
7	**6**	4-*tert*-Butyl-bromobenzene	Cs_2CO_3	Toluene	1	110	8	95	86
8	**6**	4-Bromotoluene	Cs_2CO_3	Toluene	1	110	8	92	84
9	**6**	4-Bromoanisole	Cs_2CO_3	DMA	1	135	8	68	–
10	**6**	4-Bromoacetophenone	Cs_2CO_3	Toluene	0.1	110	24	91	85
11	**6**	4-Bromoacetophenone	Cs_2CO_3	Toluene	0.01	110	48	40	–
12	**6**	4-Bromoacetophenone	Cs_2CO_3	DMA	0.1	135	24	98	92
13	**6**	4-Bromoacetophenone	Cs_2CO_3	DMA	0.01	135	48	57	–
14	**6**	4-Chloroacetophenone	Cs_2CO_3	Toluene	1	110	48	5	–
15	**6**	4-Chloroacetophenone	Cs_2CO_3	DMA	1	135	48	56	–
16	**6**	4-Chloroacetophenone	Cs_2CO_3	DMA	2	135	24	80	–

[a] Reaction conditions: 1 mmol aryl halide, 1.3 mmol styrene, 1.5 mmol base, 2 ml solvent.
[b] Determined by ^{1}H NMR.
[c] Isolated yield. (average of two experiments).

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* 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 by an Elementar Vario ELIV instrument.

Benzanilide (Lancaster), PCl_5 (RDH), 2-aminomethylpyridine (Acros), DMA (TEDIA), $Pd(OAc)_2$ (Acros), KF (Acros), K_3PO_4 (Lancaster), Cs_2CO_3 (Aldrich) and LiCl (Lancaster) were used as supplied. NEt_3 and *N*,*N*-dimethylethyleneamine were dried over CaH_2 and distilled before use. *N*-(phenyl)benzimidoyl chloride[19] and 2-(*o*-aminophenyl)oxazoline[44] were prepared by the modified literature's methods.

4.2. Preparations

4.2.1. [C_6H_5–C{NH(CH_2)$_2$NMe_2}=NC_6H_5] (1). A yellow solution of *N*-(phenyl)benzimidoyl chloride (0.81 g, 3.8 mmol) and NEt_3 (0.70 ml, 4.6 mmol) in CH_2Cl_2 (20 ml) was treated with *N*,*N*-dimethylethyleneamine (0.41 ml, 3.8 mmol) at room temperature. After 18 h of stirring, the volatiles were removed under reduced pressure and the residue was extracted with 50 ml hexane. The extract was concentrated and put into the fridge to afford white solid. Yield, 0.64 g, 63%. ^{1}H NMR (600 MHz): δ 2.25 (s, N(CH_3)$_2$, 6H), 2.57 (br, CH_2–CH_2, 2H), 3.56 (br, CH_2–CH_2, 2H), 5.29 (br, N*H*), 6.63 (d, C_6H_5, 2H, J=7.2 Hz), 6.78 (t, C_6H_5, 1H, J=7.2 Hz), 7.03 (t, C_6H_5, 2H, J=7.2 Hz), 7.22 (overlap, C_6H_5, 5H). $^{13}C\{^{1}H\}$ NMR (150 MHz): δ 39.0 (s, CH_2), 45.1 (s, N(CH_3)$_2$), 57.6 (s, CH_2), 121.0, 123.1, 128.1, 128.2, 128.6, 128.9(*C*H–C_6H_5), 135.2, 151.0, 157.7 (two C_{ipso}–C_6H_5 and one *C*NN). Anal. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72. Found: C, 76.17; H, 8.26; N, 15.22.

4.2.2. [C_6H_5–C{NHCH_2Py}=NC_6H_5] (2). A yellow solution of *N*-(phenyl)benzimidoyl chloride (1.08 g, 5.0 mmol) and NEt_3 (0.90 ml, 6 mmol) in CH_2Cl_2 (20 ml) was treated with 2-aminomethylpyridine (0.52 ml, 5.0 mmol) at room temperature. After 18 h of stirring, the volatiles were removed under reduced pressure and the residue was extracted with 15 ml toluene to afford white solid. The resulting solid was purified by ethyl acetate/hexane solution to afford white solid. Yield, 0.83 g, 58%. ^{1}H NMR (600 MHz): δ 4.87 (s, CH_2, 2H), 6.15 (br, N*H*, 1H), 6.68 (d, C_6H_5, 2H, J=6.6 Hz), 6.83 (br, C_6H_5, 1H), 7.07 (t, C_6H_5, 2H, J=7.2 Hz), 7.21 (t, C_6H_5, 1H, J=6.0 Hz), 7.25–7.31 (m, C_6H_5, 5H), 7.39 (d, C_6H_5, 1H, J=7.2 Hz), 7.70 (t, C_6H_5, 1H, J=7.2 Hz), 8.54 (d, C_6H_5, 1H, J=4.2 Hz). $^{13}C\{^{1}H\}$ NMR (150 MHz): δ 46.7 (s, CH_2), 121.3, 122.2, 122.3, 123.1, 128.2, 128.3, 128.7, 129.1, 136.6, 148.8(*C*H–C_6H_5 and *C*H–Py), 135.0, 150.7, 156.8, 157.2 (three C_{ipso}–C_6H_5 and one *C*NN). Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.53; H, 5.90; N, 14.56.

4.2.3. [C_6H_5–C{NHC_6H_4Oxazoline}=NC_6H_5] (3). To a yellow solution of *N*-(phenyl)benzimidoyl chloride (0.43 g, 2.0 mmol) and 2-(*o*-aminophenyl)oxazoline (0.38 g, 2 mmol) in CH_2Cl_2 (20 ml), NEt_3 (0.33 ml, 2.4 mmol) was added at room temperature. After 18 h of stirring, the resulting suspension was filtered at 0 °C and the volatiles were removed under reduced pressure. The residue was extracted with 50 ml hexane to afford pale-yellow solid. Yield, 0.54 g, 73%. ^{1}H NMR (600 MHz): δ 1.25 (s, CH_3, 6H), 4.02 (s, CH_2, 2H), 6.74 (d, 2H, J=7.2 Hz), 6.86 (t, 1H, J=7.2 Hz), 7.00 (t, 1H, J=7.2 Hz), 7.11 (t, 2H, J=7.2 Hz), 7.24–7.30 (m, 3H), 7.40 (d, 2H, J=7.2 Hz), 7.47 (t, 1H, J=7.2 Hz), 7.85 (d, 1H, J=7.8 Hz), 9.24 (d, 1H, J=8.4 Hz), 11.93 (s, N*H*, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz): δ 28.4 (s, CH_3), 67.7 (s, *C*-(CH_3)$_2$), 77.5 (s, CH_2), 119.3, 120.5, 121.5, 122.5, 127.8, 128.4, 128.9, 129.1, 129.2, 132.4(*C*H–Ph), 112.8, 135.2, 142.0, 150.3, 154.5, 162.0 (one *tert*-*C*-oxazoline, one *tert*-*C*-Ph, three C_{ipso}–C_6H_5 and one *C*NN). Anal. Calcd for $C_{24}H_{23}N_3O$: C, 78.02; H, 6.27; N, 11.37. Found: C, 78.08; H, 6.08; N, 11.41.

4.2.4. [C_6H_5–C{=N(CH_2)$_2$NMe_2}–NH–(η^1-C_6H_5)]Pd(OAc) (4). To a flask containing **1** (0.27 g, 1.0 mmol) and $Pd(OAc)_2$ (0.22 g, 1.0 mmol), 15 ml of CH_2Cl_2 was added at room temperature. After 18 h of stirring, the resulting mixture was layered 15 ml hexane and put into the fridge. The crystalline solid was isolated after several days. Yield, 0.21 g, 49%. ^{1}H NMR (600 MHz): δ 1.66 (s, O–C(=O)CH_3, 3H), 2.40 (t, CH_2, 2H, J=6.0 Hz), 2.61 (s, N(CH_3)$_2$, 6H), 3.18 (t, CH_2, 2H, J=6.0 Hz), 6.90 (t, C_6H_5, 1H, J=7.2 Hz), 6.99 (d, C_6H_5, 2H, J=7.2 Hz), 7.07 (t, C_6H_5, 1H, J=7.2 Hz), 7.31 (d, C_6H_5, 1H, J=7.8 Hz), 7.37–7.44 (m, C_6H_5, 4H), 9.71 (s, N*H*, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz): δ 24.1 (s, O–C(=O)CH_3), 47.9 (s, N(CH_3)$_2$), 52.5 (s, CH_2), 61.8 (s, CH_2), 117.0, 121.5, 123.6, 128.1, 128.7, 129.8, 135.4(*C*H–Ph), 126.3, 131.8, 135.9, 152.1 (two C_{ipso}–C_6H_5, one metallated *C*–Ph, and one *C*NN), 178.1 (s, O–*C*(=O)CH_3). Anal. Calcd for $C_{19}H_{23}N_3O_2Pd$: C, 52.85; H, 5.37; N, 9.73. Found: C, 52.85; H, 4.88; N, 9.48.

4.2.5. [C_6H_5–C{=NCH_2Py}–NH–(η^1-C_6H_5)]Pd(OAc) (5). To a flask containing **2** (0.29 g, 1.0 mmol) and $Pd(OAc)_2$ (0.22 g, 1.0 mmol), 15 ml of CH_2Cl_2 was added at room temperature. After 18 h of stirring, the resulting suspension was filtered and the precipitate was extracted with 30 ml cold THF. The combined organic solution was allowed to stand at room temperature to afford white solid after several days. Yield, 0.25 g, 55%. ^{1}H NMR (600 MHz): δ 1.90 (s, O–C(=O)CH_3, 3H), 4.58 (s, CH_2Py, 2H), 6.62 (m, C_6H_5 or Py, 1H), 6.84–6.88 (m, C_6H_5 or Py, 2H), 7.09 (m, C_6H_5 or Py, 2H), 7.13 (d, C_6H_5 or Py, 1H, J=7.8 Hz), 7.29 (m, C_6H_5 or Py, 1H), 7.46 (m, C_6H_5 or Py, 2H), 7.51 (m, C_6H_5 or Py, 1H), 7.56 (m, C_6H_5 or Py, 1H), 7.74 (m, C_6H_5 or Py, 1H), 8.39 (m, C_6H_5 or Py, 1H), 9.64 (s, N*H*, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz): δ 24.4 (s, O–C(=O)CH_3), 62.1 (s, CH_2), 116.4, 119.7, 121.2, 122.8, 123.9, 128.3,

128.7, 130.1, 135.4, 137.6, 148.4(*C*H of Ph or Py), 127.1, 131.9, 135.2, 152.3, 159.0 (three C_{ipso}–C_6H_5, one metallated *C*–Ph, and one *C*NN), 178.2 (s, O–*C*(=O)CH_3). Anal. Calcd for $C_{21}H_{19}N_3O_2Pd$: C, 55.82; H, 4.24; N, 9.30. Found: C, 55.79; H, 4.19; N, 9.52.

4.2.6. [C_6H_5–C{=NC_6H_4Oxazoline}–NH–(η^1-C_6H_5)] Pd(OAc) (6). To a flask containing **3** (0.65 g, 1.75 mmol) and $Pd(OAc)_2$ (0.39 g, 1.75 mmol), 15 ml of CH_2Cl_2 was added at room temperature. After 18 h of stirring, the resulting mixture was layered 15 ml hexane and put into the fridge. The crystalline solid was isolated after several days. Yield, 0.61 g, 65%. ^{1}H NMR (600 MHz): δ 1.59 (s, C(CH_3)$_2$, 3H), 1.89 (s, C(CH_3)$_2$, 3H), 1.92 (s, O–C(=O)CH_3, 3H), 4.34 (m, CH_2, 2H), 6.13 (m, C_6H_5, 1H), 6.21 (br, C_6H_5, 1H), 6.76–6.87 (overlap, C_6H_5, 4H), 7.16 (t, C_6H_5, 2H, J=7.8 Hz), 7.24 (m, C_6H_5, 1H), 7.29 (d, C_6H_5, 2H, J=7.2 Hz), 7.64 (m, C_6H_5, 1H), 8.58 (br, C_6H_5, 1H), 10.10 (s, N*H*, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 25.2 (s, O–C(=O)*C*H_3), 27.8 (s, C(*C*H_3)$_2$), 28.9 (s, C(*C*H_3)$_2$), 69.3 (s, *C*(CH$_3$)$_2$), 80.7 (s, *C*H$_2$), 122.9, 123.8, 124.0, 127.5, 128.6, 128.9, 130.2, 131.4, 131.6, 133.6, 135.0(C_6H_5), 117.8, 119.7, 126.2, 132.5, 147.9, 156.2, 161.2 (one *tert-C*-oxazoline, one *tert-C*-Ph, three C_{ipso}–C_6H_5, one metallated *C*-Ph, and one *C*NN), 178.0 (s, O–*C*(=O)CH_3). Anal. Calcd for d$C_{26}H_{25}N_3O_3Pd$: C, 58.49; H, 4.72; N, 7.87. Found: C, 58.28; H, 4.81; N, 7.58.

4.2.7. [C_6H_5–C{=N$(CH_2)_2NMe_2$}–NH–(η^1-C_6H_5)]PdCl (7). To a flask containing **4** (0.22 g, 0.5 mmol) and LiCl (0.085 g, 2.0 mmol), 15 ml of $CHCl_3$ was added at room temperature. After 18 h of stirring, the resulting mixture was filtered and layered 15 ml hexane. The white solid was isolated after several days. Yield, 0.16 g, 82%. ^{1}H NMR (600 MHz): δ 2.50 (t, CH_2, 2H, J=6.0 Hz), 2.72 (s, N(CH_3)$_2$, 6H), 3.47 (t, CH_2, 2H, J=6.0 Hz), 6.61 (m, C_6H_5, 1H), 6.88 (m, C_6H_5, 1H), 7.00 (m, C_6H_5, 1H), 7.02 (s, N*H*, 1H), 7.40 (m, C_6H_5, 2H), 7.55–7.59 (overlap, C_6H_5, 3H), 8.44 (m, C_6H_5, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 48.2 (s, N(*C*H_3)$_2$), 53.4 (s, *C*H$_2$), 62.5 (s, *C*H$_2$), 115.1, 122.6, 125.0, 127.2, 129.6, 130.9, 141.1(*C*H–Ph), 123.6, 132.6, 134.1, 151.6 (two C_{ipso}–C_6H_5, one metallated *C*-Ph, and one *C*NN). Anal. Calcd for $C_{17}H_{20}ClN_3Pd$: C, 50.02; H, 4.94; N, 10.29. Found: C, 50.11; H, 4.84; N, 9.92.

4.2.8. [C_6H_5–C{=NCH_2Py}–NH–(η^1-C_6H_5)]PdCl (8). To a flask containing **5** (0.23 g, 0.5 mmol) and LiCl (0.085 g, 2.0 mmol), 15 ml of $CHCl_3$ was added at room temperature. After 18 h of stirring, the resulting mixture was filtered and layered 15 ml hexane. The white solid was isolated after several days. Yield, 0.16 g, 71%. ^{1}H NMR (600 MHz): δ 4.88 (s, CH_2Py, 2H), 6.68 (m, C_6H_5 or Py, 1H), 6.95 (m, C_6H_5 or Py, 1H), 7.06 (m, C_6H_5 or Py, 1H), 7.17 (d, C_6H_5 or Py, 1H, J=7.8 Hz), 7.18 (s, N*H*, 1H), 7.34 (t, C_6H_5 or Py, 1H, J=6.6 Hz), 7.46 (m, C_6H_5 or Py, 2H), 7.60–7.65 (m, C_6H_5 or Py, 3H), 7.74 (m, C_6H_5 or Py, 1H), 8.52 (d, C_6H_5 or Py, 1H, J=7.8 Hz), 9.37 (d, C_6H_5 or Py, 1H, J=4.8 Hz). ^{13}C{^{1}H} NMR (150 MHz): δ 62.8 (s, *C*H$_2$), 115.3, 119.6, 122.8, 123.1, 125.1, 127.1, 129.8, 131.1, 137.8, 141.2, 149.6(*C*H of Ph or Py), 125.6, 132.4, 133.6, 152.4, 158.7 (three C_{ipso}–C_6H_5, one metallated *C*–Ph, and one *C*NN), Anal. Calcd for $C_{19}H_{16}ClN_3Pd$: C, 53.29; H, 3.77; N, 9.81. Found: C, 52.91; H, 4.33; N, 9.43.

4.2.9. [C_6H_5–C{=NC_6H_4Oxazoline}–NH–(η^1-C_6H_5)] PdCl (9). To a flask containing **6** (0.53 g, 0.5 mmol) and LiCl (0.17 g, 4.0 mmol), 15 ml of $CHCl_3$ was added at room temperature. After 18 h of stirring, the resulting mixture was filtered and the volatiles were removed under reduced pressure. The crude product was recrystallized from $CHCl_3$/hexane to afford yellow solid after several days. Yield, 0.38 g, 75%. ^{1}H NMR (600 MHz): δ 1.81 (s, C(CH_3)$_2$, 3H), 1.87 (s, C(CH_3)$_2$, 3H), 4.18 (d, CH_2, 1H, J=7.8 Hz), 4.38 (d, CH_2, 1H, J=8.4 Hz), 6.27 (d, C_6H_5, 1H, J=7.8 Hz), 6.91 (t, C_6H_5, 2H, J=7.8 Hz), 6.98 (t, C_6H_5, 1H, J=7.8 Hz), 7.03 (t, C_6H_5, 1H, J=7.8 Hz), 7.10 (d, C_6H_5, 1H, J=7.8 Hz), 7.29 (overlap, C_6H_5, 2H), 7.33 (t, C_6H_5, 2H, J=7.8 Hz), 7.41 (t, C_6H_5, 1H, J=7.8 Hz), 7.74 (m, C_6H_5, 2H), 8.18 (s, N*H*, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 27.5 (s, C(*C*H_3)$_2$), 28.6 (s, C(*C*H_3)$_2$), 70.7 (s, *C*(CH$_3$)$_2$), 81.2 (s, *C*H$_2$), 115.0, 124.2, 124.3, 125.2, 127.6, 129.1, 129.2, 130.2, 131.7, 132.2, 139.9(C_6H_5), 120.9, 126.0, 133.5, 146.4, 156.5, 161.1 (one *tert-C*-oxazoline, one *tert-C*-Ph, three C_{ipso}–C_6H_5, one metallated *C*–Ph, and one *C*NN; one *tert-C* is missed). Anal. Calcd for $C_{24}H_{22}ClN_3OPd$: C, 56.49; H, 4.35; N, 8.23. Found: C, 55.32; H, 4.07; N, 7.95.

4.3. 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 80 °C for the prescribed time. After removal of the volatiles, the residue was diluted with ethyl acetate, filtered through a pad of silica gel. A sample in chloroform-*d* was taken for determination of conversion. The crude material was further purified by flash chromatography on silica gel.

4.4. General procedure for the Heck reaction

Prescribed amount of catalyst, base (1.5 equiv) and aryl halide (1 equiv) were placed in a Schlenk tube under nitrogen. Solvent (2 ml) and styrene (1.3 equiv) were added by syringe, and the reaction mixture was heated to the prescribed temperature for the prescribed time. After removal of the volatiles, the residue was diluted with ethyl acetate, filtered through a pad of silica gel. A sample in chloroform-*d* was taken for determination of conversion. The crude material was further purified by flash chromatography on silica gel.

4.5. Crystal structure data

Crystals were grown from concentrated hexane solution (**1**), toluene/hexane solution (**3**), concentrated dichloromethane solution (**5**), or CH_2Cl_2/hexane solution (**6** and **7**), and isolated by filtration. Suitable crystals of **1**, **3**, **5**, **6** or **7** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure

Table 8. Summary of crystal data for compounds **1**, **3**, **5**, **6** and **7**

	1	**3**	**5**	**6**	**7**
Formula	$C_{17}H_{21}N_3$	$C_{48}H_{46}N_6O_2$	$C_{21}H_{19}N_3O_2Pd$	$C_{27.50}H_{27}Cl_3N_3O_3Pd$	$C_{34}H_{40}Cl_2N_6Pd_2$
Fw	267.37	738.91	451.79	660.27	816.42
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	P-1	P-1	C2/c	$P2_12_12_1$
a (Å)	9.720(2)	10.4288(10)	9.6436(11)	24.6826(13)	12.2320(11)
b (Å)	11.651(3)	10.5934(11)	10.6773(12)	16.8272(9)	16.2444(14)
c (Å)	14.041(3)	18.6013(17)	10.8489(12)	14.1632(7)	17.1797(15)
α (°)	90	81.271(2)	109.326(2)	90	90
β (°)	92.599(5)	89.850(2)	96.282(2)	95.7540(10)	90
γ (°)	90	83.956(2)	113.133(2)	90	90
V (Å^3)	1588.5(6)	2019.7(3)	931.75(18)	5852.9(5)	3413.6(5)
Z	4	2	2	8	4
ρ_{calc} (Mg/m^3)	1.118	1.215	1.610	1.499	1.589
μ(Mo Kα) (mm^{-1})	0.067	0.076	1.017	0.941	1.243
Reflections collected	8826	11,567	5321	16,382	19,226
No. of parameters	207	505	244	339	397
$R1$[a]	0.0661	0.0486	0.0352	0.0400	0.0359
w$R2$[a]	0.1818	0.1062	0.0969	0.1191	0.0965
GoF[b]	0.928	1.020	0.798	0.934	0.765

[a] $R1=[(|F_0|-|F_c|)/|F_0|]$; w$R2=[\ w(F_0^2-F_c^2)^2/\ w(F_0^2)^2]^{1/2}$, $w=0.10$.
[b] Go$F=[w(F_0^2-F_c^2)^2/(N_{rflns}-N_{params})]^{1/2}$.

was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 8.

5. Supplementary information

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers, CCDC no. 248112–248116 for compounds **1**, **3**, **5**, **6** and **7**, respectively. Copies of this information can be obtained, free of charge, from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or email:deposit@ccdc.cam.ac.uk].

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