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Palladacyclic Complexes Containing C,N-Type Ligands as Catalysts in Cross-Coupling Reactions

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Four ligand precursors, namely PhN=C(CMe_2)(NPh)C=N(E) [E = –(CH_2)$_2$OMe (**1**); –(CH_2)C(O)OMe (**2**); –(CH_2)$_2$$CH_3$ (**3**); –C_6H_5 (**4**)], are described. Treatment of **1**, **2**, **3** or **4** with 1–1.1 molar equivalents of Pd(OAc)$_2$ in THF or CH_3CN affords the orthometallated palladium(II) complexes [{[PhN=C(CMe_2)-(N-η^1-Ph)C=N(E)]Pd(OAc)}$_2$] [E = –(CH_2)$_2$OMe (**5**); –(CH_2)-C(O)OMe (**6**); –(CH_2)$_2$$CH_3$ (**7**); –C_6H_5 (**8**)], respectively. The reaction of **5** or **6** with an excess of NaCl(aq.) in acetone affords the orthometallated palladium(II) complexes [{PhN=C(CMe_2)(N-η^1-Ph)C=N(E)}PdCl] [E = –(CH_2)$_2$OMe (**9**); –(CH_2)C(O)OMe (**10**)], whereas the reaction of **7** with an excess of NaCl(aq.) in acetone affords the dinuclear palladium(II) complex [{[PhN=C(CMe_2)(N-η^1-Ph)C=N(CH_2)$_2$$CH_3$]-PdCl}$_2$] (**11**). The crystal and molecular structures of compounds **2**, **4**, **5**, **7**, **8** and **9** are reported The application of those novel palladacyclic complexes to the Suzuki and Heck reactions with aryl halide substrates is examined.

Introduction

Palladium-catalyzed cross-coupling reactions have attracted a great deal of attention during the past few decades mainly due to their widespread application in the formation of carbon–carbon bonds between aryl or alkyl and aryl groups.[1–15] Palladacycles bearing a metallated carbon atom seem to be the most active catalyst precursors for the promotion of such reactions,[1–6,8–10,12,14,15] therefore potential ancillary ligands that can serve as cyclometallated precursors are of current interest. The most common palladium(II) complexes reported in the literature are five-membered ring palladacyclic species. Those complexes usually form dinuclear species with bridged ligands or mono-nuclear species in the presence of a neutral donor group. We have recently reported some six-membered ring palladacycles.[16,17] The successful application of these complexes in catalytic cross-coupling reactions encouraged us to study the catalytic performance exhibited by palladacycles with other functionalities. Following our previous work on four-membered ring diimino palladacycles,[17] we report here the synthesis and characterisation of novel palladacycles supported by different functionalities. Their catalytic activities towards Suzuki and Heck reactions are also discussed.

Results and Discussion

Syntheses and Characterisation of Ligand Precursors and Palladacycles

Four new ligand precursors **1**–**4** were synthesized from the reaction of 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride with the appropriate amine or amine hydrochloride (2-methoxyethylamine for **1**, glycine methyl ester hydrochloride for **2**, propylamine for **3**, aniline for **4**) in the presence of excess NEt_3 using a similar procedure to that reported in the literature.[17] Compounds **1**–**4** were characterised by NMR spectroscopy and elemental analysis, which indicated four-membered ring diimine compounds with different functionalities. A summary of the syntheses and proposed structures is shown in Scheme 1. The X-ray structures of **2** and **4** show four-membered diimine compounds bearing different pendant functionalities. Their molecular structures are depicted in Figures 1 and 2, respectively. The bond lengths and bond angles around the imino C and N atoms are indicative of significant double bond character and an sp^2 character of the carbon centres.

Treatment of **1**, **2**, **3** or **4** with one molar equivalent of Pd(OAc)$_2$ at room temperature or under reflux yielded complexes **5**, **6**, **7** or **8**, respectively, in high yield. Similar to the results reported previously, signals correlating to the metallated carbon atom were found in the $^{13}C\{^1H\}$ NMR spectra in each case, thus indicating the formation of palladacycles. Only one signal corresponding to the OAc ligand is observed in the NMR spectra of those OAc-containing palladacycles, thereby indicating an *anti* configuration,[18a,18b] which is consistent with the observation in the solid state.

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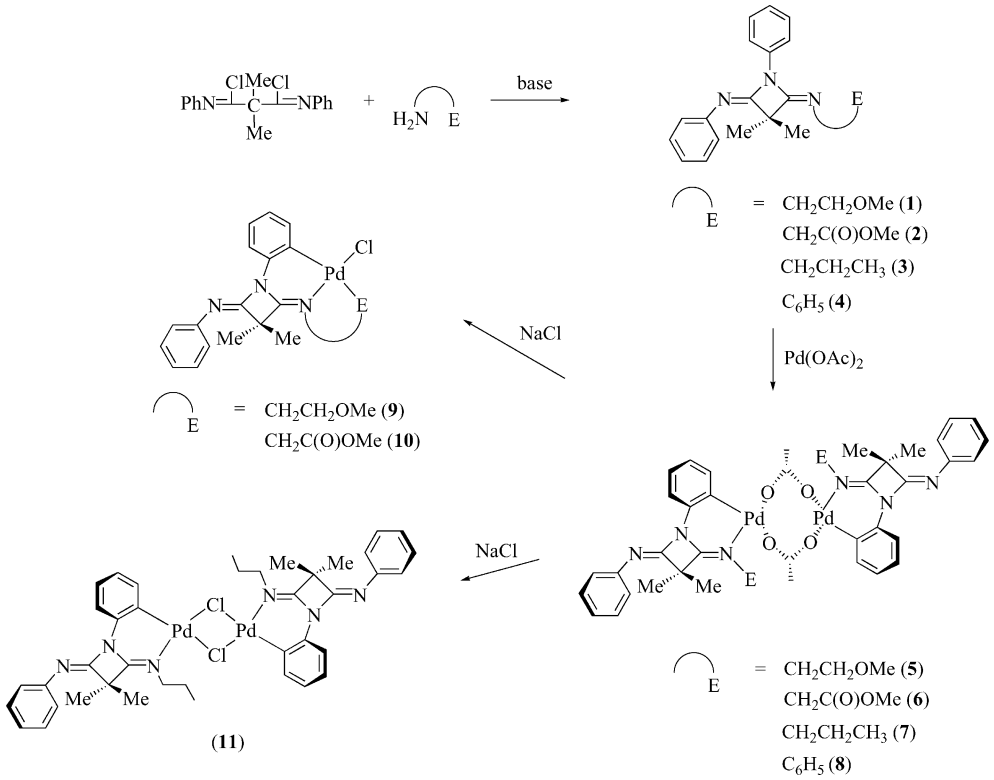


Scheme 1.

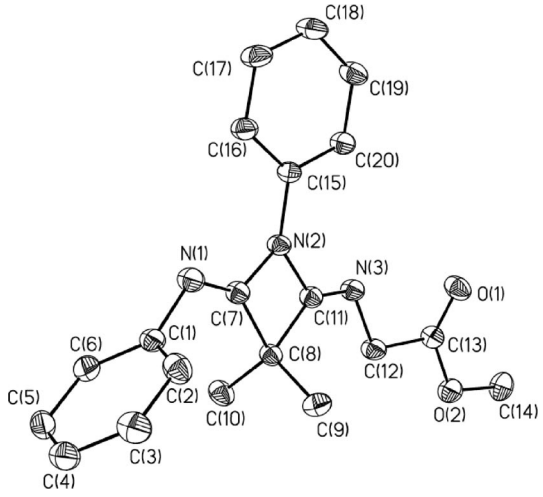


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and bond angles [°]: N(1)–C(1) 1.427(3), N(3)–C(11) 1.256(3), N(1)–C(7) 1.262(3), N(2)–C(15) 1.417(3), N(2)–C(7) 1.403(3), N(3)–C(12) 1.456(3), N(2)–C(11) 1.411(3); N(1)–C(7)–N(2) 128.4(2), N(3)–C(11)–C(8) 140.6(2), N(1)–C(7)–C(8) 139.6(2), N(2)–C(11)–C(8) 91.34(18), N(2)–C(7)–C(8) 91.92(18), C(7)–N(1)–C(1) 120.5(2), C(7)–C(8)–C(11) 83.20(18), C(11)–N(3)–C(12) 116.3(2), N(3)–C(11)–N(2) 128.1(2). Hydrogen atoms on carbon atoms have been omitted for clarity.

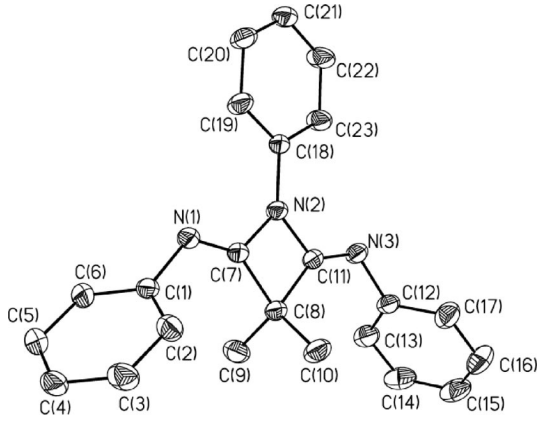


Figure 2. Molecular structure of **4**. Selected bond lengths [Å] and bond angles [°]: N(1)–C(1) 1.424(3), N(3)–C(11) 1.261(3), N(1)–C(7) 1.251(3), N(2)–C(18) 1.418(3), N(2)–C(7) 1.409(3), N(3)–C(12) 1.420(3), N(2)–C(11) 1.403(3); N(1)–C(7)–N(2) 126.98(19), N(3)–C(11)–C(8) 140.9(2), N(1)–C(7)–C(8) 141.89(19), N(2)–C(11)–C(8) 91.93(16), N(2)–C(7)–C(8) 91.02(16), C(7)–N(1)–C(1) 121.99(19), C(7)–C(8)–C(11) 83.48(15), C(11)–N(3)–C(12) 121.1(2), N(3)–C(11)–N(2) 127.1(2). Hydrogen atoms on carbon atoms have been omitted for clarity.

Crystals of **5**, **7** and **8** suitable for a structural determination were obtained from CH_2Cl_2/hexane solution. The molecular structures are depicted in Figures 3, 4 and 5, respectively. These palladacycles are found to be dinuclear species with two acetates as bridging ligands. Each palladium atom is coordinated in a slightly distorted square-planar geometry to one phenyl ring carbon atom, one imine nitrogen atom and two bridging acetate oxygen atoms. The N–Pd–$C_{metallated}$ bite angles [92.98(11)° for **5**; 93.10(11)° and 93.76(11)° for **7**; 91.78(14)° and 92.71(14)° for **8**] resulting from the imino nitrogen and the metallated carbon are similar to those [93.20(10)°, 93.77(8)°, 94.51(10)°, and 93.47(12)°] found in our previous work.[17] The Pd–$C_{metallated}$ bond lengths [1.984(3) Å for **5**; 1.995(3) and

2.002(3) Å for **7**; 1.988(4) and 2.004(4) Å for **8**] are similar to those found in related palladacycles with a metallated carbon atom [1.948(4)–2.061(3) Å].[16,17,19] The Pd–$N_{C=N}$ bond lengths [2.020(3) Å for **5**; 2.015(3) and 2.024(3) Å for **7**; 2.030(3) and 2.021(3) Å for **8**] are also similar to those found in other palladacycles [1.981(3)–2.111(4) Å].[16,17,19a,19d,19e,19h–19j] The Pd–O_{OAc} bond lengths [2.037(2) and 2.143(2) Å for **5**; 2.048(2), 2.142(2), 2.048(2) and 2.158(2) Å for **7**; 2.041(3), 2.126(3), 2.042(3) and 2.131(3) Å for **8**] are similar to those found in the literature [2.033(3)–2.160(3) Å].[19e,19f,20,21] Due to the *trans* influence of the nitrogen atoms, the palladium–oxygen bonds are shorter than those *trans* to the palladium–carbon bonds.

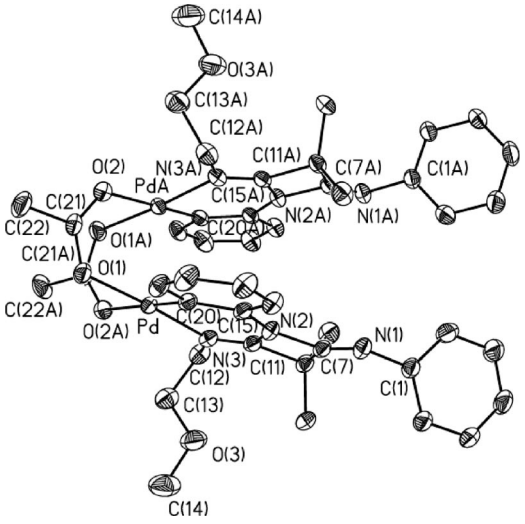


Figure 3. Molecular structure of **5**. Selected bond lengths [Å] and bond angles [°]: Pd–Pd(A) 2.9289(7), Pd–C(20) 1.984(3), Pd–N(3) 2.020(3), Pd–O(1) 2.037(2), Pd–O(2A) 2.143(2), C(15)–C(20) 1.392(4), C(15)–N(2) 1.406(4), N(3)–C(11) 1.254(4); C(20)–Pd–N(3) 92.98(11), C(20)–Pd–O(1) 91.16(11), N(3)–Pd–O(1) 175.32(11), C(20)–Pd–O(2A) 173.86(11), N(3)–Pd–O(2A) 92.24(10), O(1)–Pd–O(2A) 83.50(10). Hydrogen atoms on carbon atoms have been omitted for clarity.

The reactions of **5**, **6** or **7** with an excess of aqueous sodium chloride in acetone at room temperature yielded **9**, **10** or **11**, respectively, as yellow solids.[21] Compounds **9**–**11** were characterized by NMR spectroscopy and elemental analysis. Crystals of **9** suitable for a structural determination were obtained from concentrated chloroform solution. The molecular structure is shown in Figure 6. Compound **9** is mononuclear with a coordinated Cl instead of OAc for those palladacycles with tridentate ligands, whereas compound **11** is a dinuclear species with two chlorides as bridging ligands due the lack of pendant functionality. The bond lengths and bond angles are similar to those discussed above The Pd–Cl bond length [2.3158(8) Å] is at the lower end of those [2.3181(2)–2.3999(7) Å] found for palladacycles containing tridentate ligands.[17a,19a,19f–19h,19k] The Pd–O_{OMe} bond length [2.204(2) Å] is similar to those [2.192(4)–2.276(3) Å] found for other palladacycles.[22]

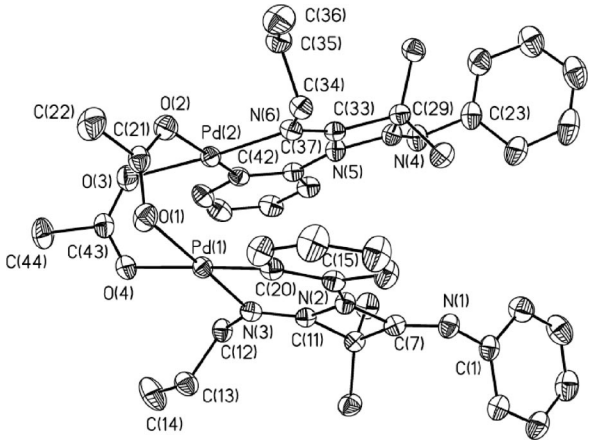


Figure 4. Molecular structure of **7**. Selected bond lengths [Å] and bond angles [°]: Pd(1)–Pd(2) 2.9409(4), Pd(1)–C(20) 1.995(3), Pd(2)–C(42) 2.002(3), Pd(1)–N(3) 2.015(3), Pd(2)–N(6) 2.024(3), Pd(1)–O(1) 2.048(2), Pd(2)–O(2) 2.158(2), Pd(1)–O(4) 2.142(2), Pd(2)–O(3) 2.048(2), C(15)–C(20) 1.389(4), C(42)–C(37) 1.402(4), C(15)–N(2) 1.415(4), C(37)–N(5) 1.415(4), N(3)–C(11) 1.258(4), N(6)–C(33) 1.265(4); C(20)–Pd(1)–N(3) 93.10(11), C(42)–Pd(2)–N(6) 93.76(11), C(20)–Pd(1)–O(1) 90.48(12), C(42)–Pd(2)–O(3) 91.41(12), N(3)–Pd(1)–O(1) 176.31(10), N(6)–Pd(2)–O(3) 174.45(10), C(20)–Pd(1)–O(4) 173.24(11), C(42)–Pd(2)–O(2) 172.04(11), N(3)–Pd(1)–O(4) 92.32(10), N(6)–Pd(2)–O(2) 92.17(10), O(1)–Pd(1)–O(4) 84.17(11), O(3)–Pd(2)–O(2) 82.50(11). Hydrogen atoms on carbon atoms have been omitted for clarity.

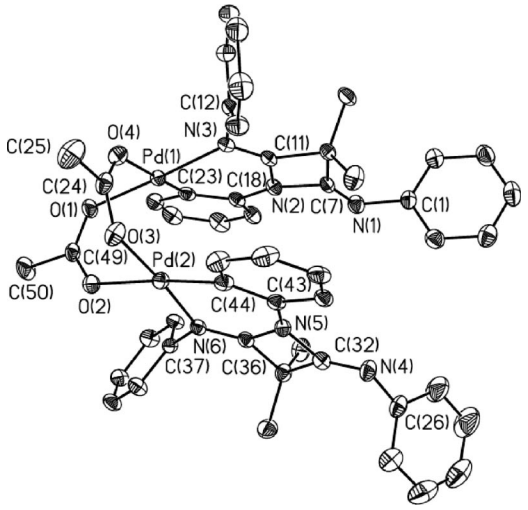


Figure 5. Molecular structure of **8**. Selected bond lengths [Å] and bond angles [°]: Pd(1)–Pd(2) 3.0818(8), Pd(1)–C(23) 1.988(4), Pd(2)–C(44) 2.004(4), Pd(1)–N(3) 2.030(3), Pd(2)–N(6) 2.021(3), Pd(1)–O(1) 2.041(3), Pd(2)–O(2) 2.131(3), Pd(1)–O(4) 2.126(3), Pd(2)–O(3) 2.042(3), C(18)–C(23) 1.387(5), C(43)–C(44) 1.394(5), C(18)–N(2) 1.427(5), C(43)–N(5) 1.422(5), N(3)–C(11) 1.274(5), N(6)–C(36) 1.268(5); C(23)–Pd(1)–N(3) 91.78(14), C(44)–Pd(2)–N(6) 92.71(14), C(23)–Pd(1)–O(1) 89.39(14), C(44)–Pd(2)–O(3) 89.94(14), N(3)–Pd(1)–O(1) 178.06(12), N(6)–Pd(2)–O(3) 175.68(13), C(23)–Pd(1)–O(4) 174.37(14), C(44)–Pd(2)–O(2) 172.49(14), N(3)–Pd(1)–O(4) 91.47(12), N(6)–Pd(2)–O(2) 90.16(11), O(1)–Pd(1)–O(4) 87.23(12), O(2)–Pd(2)–O(3) 86.81(12). Hydrogen atoms on carbon atoms have been omitted for clarity.

Attempts to synthesize a palladium chloride complex containing ligand **4** by a similar route proved unsuccessful due to the poor solubility of the products.

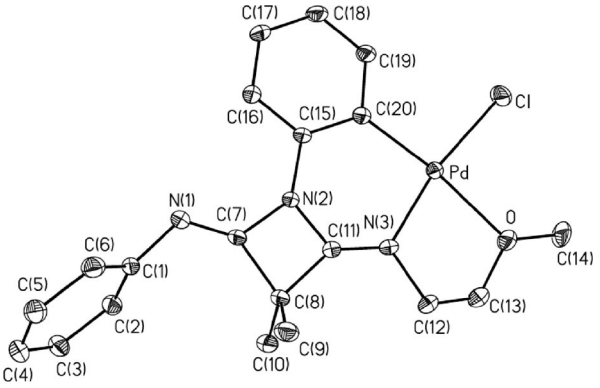
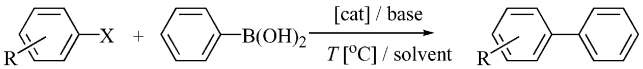


Figure 6. Molecular structure of **9**. Selected bond lengths [Å] and bond angles [°]: Pd–C(20) 1.996(3), N(2)–C(15) 1.423(3), Pd–O 2.204(2), Pd–Cl 2.3158(8), N(1)–C(7) 1.252(4), Pd–N(3) 2.008(2); C(20)–Pd–N(3) 93.85(11), C(20)–Pd–Cl 96.47(8), N(3)–Pd–O 78.51(10), O–Pd–Cl 91.16(6), C(20)–Pd–O 172.33(10), N(3)–Pd–Cl 169.59(7). Hydrogen atoms on carbon atoms have been omitted for clarity.

Catalytic Studies

With the aim of comparing the reactivity of these complexes with related C,N-type palladacycles, we chose the Suzuki reaction, as shown in Scheme 2. The potential catalyst precursors **5**–**11** were tested in the coupling of 4-bromoacetophenone with phenylboronic acid at room temperature within 1 h on a 1 mol-% scale. The optimised conditions were found to be K_3PO_4/DMA for **5** and **9** (entries 1 and 5), K_3PO_4/toluene for **6**, **10** and **11** (entries 2, 6 and 7), and KF/THF for **7** and **8** (entries 3 and 4). Selected results are listed in Table 1. Compounds **7** and **8** exhibited better activities after testing palladacycles **6**–**9** and **11** with an electronically deactivated aryl bromide under the optimised conditions (entries 8–12). Both compounds also showed catalytic activities in the reaction with he electronically activated aryl chloride with a 1 mol-% catalyst loading, although poor conversions were observed after 2 or 3 h (entries 13–14). A similar reaction with 2 mol-% catalyst loading was applied to examine the electronically deactivated aryl chloride. Poor conversion was found after 12 h (entry 15).



[cat] =palladacycles

Scheme 2. Application of the palladacycles in the Suzuki reaction.

In order to examine the catalytic activity in alcoholic solvents,[23] compound **8**, which was found to be a better precatalyst, was tested in three alcoholic solvents and water. Excellent conversions were observed within 20 min in the three alcohols and 30 min in water (entries 16–19). Due to the improvement of catalytic activities in the cross-coupling by the biphasic system,[24] compounds **7** and **8** were used to examine the catalytic activities with an electronically deactivated aryl bromide with 1 mol-% catalyst loading and an optimized volume ratio of DMF/H_2O (1:1; entries 20 and 21). The conversions were up to 99% within 15 min in both cases. This improvement encouraged us to examine the catalytic activities of both compounds with an electronically activated aryl chloride. Compound **8** exhibited better con-

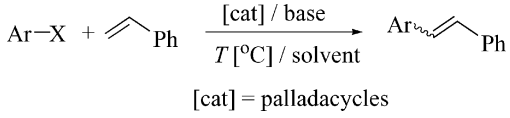
Table 1. Suzuki coupling reaction catalyzed by new palladium complexes.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] [mol-%]	*T* [h]	Conv. [%][b]	Yield [%][c]
1	**5**	4-bromoacetophenone	K_3PO_4	DMA	1	1	84	79
2	**6**	4-bromoacetophenone	K_3PO_4	toluene	1	1	99	97
3	**7**	4-bromoacetophenone	KF	THF	1	1	99	95
4	**8**	4-bromoacetophenone	KF	THF	1	1	99	96
5	**9**	4-bromoacetophenone	K_3PO_4	DMA	1	1	99	94
6	**10**	4-bromoacetophenone	K_3PO_4	toluene	1	1	67	–
7	**11**	4-bromoacetophenone	K_3PO_4	toluene	1	1	99	93
8	**6**	4-bromoanisole	K_3PO_4	toluene	1	2	95	90
9	**7**	4-bromoanisole	KF	THF	1	1.75	96	93
10	**8**	4-bromoanisole	KF	THF	1	1.75	95	91
11	**9**	4-bromoanisole	K_3PO_4	DMA	1	3	42	–
12	**11**	4-bromoanisole	K_3PO_4	toluene	1	3	33	–
13	**7**	methyl 4-chlorobenzoate	KF	THF	1	2	20	–
14	**8**	methyl 4-chlorobenzoate	KF	THF	1	3	73	–
15	**8**	4-chloroanisole	KF	THF	2	12	65	–
16	**8**	4-bromoanisole	Cs_2CO_3	MeOH	1	20 min	99	94
17	**8**	4-bromoanisole	K_3PO_4	EtOH	1	20 min	94	89
18	**8**	4-bromoanisole	K_3PO_4	IPA	1	20 min	99	95
19	**8**	4-bromoacetophenone	Cs_2CO_3	H_2O	1	30 min	88	86
20[d]	**8**	4-bromoanisole	Cs_2CO_3	DMF/H_2O	1	15 min	99	96
21[d]	**7**	4-bromoanisole	Cs_2CO_3	DMF/H_2O	1	15 min	99	94
22[d]	**7**	methyl 4-chlorobenzoate	Cs_2CO_3	DMF/H_2O	1	3	77	73
23[d]	**8**	methyl 4-chlorobenzoate	Cs_2CO_3	DMF/H_2O	1	1.5	94	88
24[d]	**8**	4-chloroanisole	Cs_2CO_3	DMF/H_2O	1	90	84	78
25[d,e]	**8**	4-chloroanisole	Cs_2CO_3	DMF/H_2O	3	4	90	85

[a] Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol phenylboronic acid, 2 mmol base, 2 mL solvent, room temperature. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield (average of two experiments). [d] Volume ratio = 1:1. [e] 60 °C.

version within 1.5 h under the same conditions (entries 22 and 23). Similar conditions were applied to examine the electronically deactivated aryl chloride. A similar conversion was obtained after 90 h (entry 24), although a higher conversion can be achieved within 4 h with 3 mol-% catalyst loading at 60 °C (entry 25). Compared with our previous work on palladacycles containing a four-membered diimine system,[17b] the CN-type palladacycles in this report demonstrate better catalytic activities for the Suzuki reaction. Under the optimised conditions, the dinuclear palladacycle **8** exhibits comparable catalytic activities in both alcoholic and biphasic systems compared with those found in the literature.[23,24] In some cases, compound **8** even shows a higher activity.

Compounds **5**–**11** were also examined as pre-catalysts in the Heck coupling reaction of 4-bromoanisole with styrene at 135 °C within 5 h on 1 mol-% Pd scale, as shown in Scheme 3. The optimised conditions were found to be K_3PO_4/DMA for **5**, **6** and **11** (entries 1, 2 and 7), K_3PO_4/DMF for **7** and **10** (entries 3 and 6), Cs_2CO_3/DMF for **8** (entry 4) and Cs_2CO_3/DMA for **9** (entry 5). Selected results are listed in Table 2. The optimised conditions were used to examine the catalytic activities of pre-catalysts **6**–**11** with an electronically activated aryl chloride with 1 mol-% catalyst loading within 12 h (entries 8–13). Due to the better conversion exhibited by **9** (entry 11), this complex was chosen to examine the catalytic activities with electronically activated (entry 14) or electronically deactivated cases (entries 15 and 16). Good conversions were obtained within 1–5 h. A lower



Scheme 3. Application of the palladacycles in the Heck reaction.

catalyst concentration (catalyst/substrate ratio of 10^{-3}) led to a conversion of 95% within 3 h (entry 17), whereas a catalyst/substrate ratio of 10^{-6} gave a turnover of up to 5.5×10^5 during a 48 h period for the coupling of an electronically activated aryl bromide (entry 18).

An enhancement of conversion was observed upon adding 1 mmol tetra-*n*-butylamine bromide (*n*-Bu_4NBr, TBAB) as co-catalyst (entries 11 and 19).[25] The same conditions were applied to the reaction with an electronically deactivated aryl chloride, with conversions of up to 94% within 24 h on 2 mol-% catalyst scale (entry 20). Compared with our previous work on palladacycles containing a four-membered diimine system,[17] palladacycle **9** demonstrates better catalytic activities than those with different functionalities for the Heck reaction. Under optimised conditions, compound **9** exhibits comparable activity in catalysing electronically deactivated aryl chloride with styrene, although with lower amounts of TBAB compared with some palladacycles.[12,15]

In summary, seven novel palladacycles bearing different functionalities have been prepared and have demonstrated catalytic activities for the Suzuki and Heck C–C coupling reactions. Under optimised conditions, the dinuclear palladacycle **8** exhibits better catalytic activities in the Suzuki coupling reaction whereas the mononuclear palladacycle **9** exhibits better catalytic activities in the Heck coupling reaction. A dramatic increase in activity was observed for the Suzuki coupling reaction when using a biphasic system. The pre-catalyst also shows excellent activity in catalysing the reaction between an electronically deactivated aryl chloride and phenylboronic acid under mild conditions. For the Heck coupling reaction, complex **9** demonstrates comparable activity in catalysing the reaction between an electronically deactivated aryl chloride and styrene at 135 °C. This might be due to the thermal stability of palladacycles with

Table 2. Heck coupling reaction catalyzed by new palladium complexes.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] [mol-%]	*T* [h]	Conv. [%][b]	Yield [%][c]
1	**5**	4-bromoanisole	K_3PO_4	DMA	1	5	62	–
2	**6**	4-bromoanisole	K_3PO_4	DMA	1	5	97	90
3	**7**	4-bromoanisole	K_3PO_4	DMF	1	5	97	91
4	**8**	4-bromoanisole	Cs_2CO_3	DMF	1	5	99	95
5	**9**	4-bromoanisole	Cs_2CO_3	DMA	1	5	97	92
6	**10**	4-bromoanisole	K_3PO_4	DMF	1	5	92	87
7	**11**	4-bromoanisole	K_3PO_4	DMA	1	5	89	83
8	**6**	4-chloroacetophenone	K_3PO_4	DMA	1	12	44	–
9	**7**	4-chloroacetophenone	K_3PO_4	DMF	1	12	26	–
10	**8**	4-chloroacetophenone	Cs_2CO_3	DMF	1	12	20	–
11	**9**	4-chloroacetophenone	Cs_2CO_3	DMA	1	12	62	–
12	**10**	4-chloroacetophenone	K_3PO_4	DMF	1	12	33	–
13	**11**	4-chloroacetophenone	K_3PO_4	DMA	1	12	28	–
14	**9**	4-bromoacetophenone	Cs_2CO_3	DMA	1	1	98	92
15	**9**	4-bromotoluene	Cs_2CO_3	DMA	1	3.5	95	90
16	**9**	4-bromoanisole	Cs_2CO_3	DMA	1	5	97	92
17	**9**	4-bromoacetophenone	Cs_2CO_3	DMA	0.1	3	95	90
18	**9**	4-bromoacetophenone	Cs_2CO_3	DMA	0.0001	48	55	–
19[d]	**9**	4-chloroacetophenone	Cs_2CO_3	DMA	1	12	91	86
20[d]	**9**	4-chloroanisole	Cs_2CO_3	DMA	2	24	94	90

[a] Reaction conditions: 1.0 mmol aryl halide, 1.3 mmol styrene, 1.5 mmol base, 2 mL solvent, 135 °C. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield (average of two experiments). [d] 1 mmol of NBu_4Br added.

terdentate ligands. Preliminary studies on fine-tuning the ligands and further application of these metal complexes to catalytic reactions are currently underway.

Experimental Section

General: All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or dry-box techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Methanol, ethanol, isopropyl alcohol, acetone, DMA (dimethyl acetamide) and DMF (dimethyl foramide) were used as supplied. Deuterated solvents were dried with molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with either a Varian Mercury-400 (400 MHz) or a Varian Inova-600 (600 MHz) spectrometer in [D]chloroform at ambient temperature unless stated otherwise. The spectra were 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. Mass spectra were recorded with a Finnigan/Thermo Quest MAT 95XL spectrometer.

Propylamine (Acros), 2-methoxyethylamine (Acros), glycine (RDH), aniline (Acros), tetra-*n*-butylammonium bromide (TCI), and $Pd(OAc)_2$ (Acros) were used as supplied. NEt_3 was dried with CaH_2 and distilled before use. 2,2-Dimethyl-*N*,*N*′-diphenylmalonamide and 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride were prepared by a literature method.[17]

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=N(CH$_2$)$_2$OMe(C^A–N^B)(C^B–C^C) (1): 2-Methoxyethylamine (1.1 mL, 12 mmol) was added to a flask containing 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (1.27 g, 4.0 mmol) and NEt_3 (2.23 mL, 16 mmol) in 40 mL of CH_2Cl_2 at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. After 14 h of stirring, the volatiles were pumped off and the residue was extracted with 30 mL of hexane to afford a white solid. Yield: 0.99 g (77.3%). ^{1}H NMR (600 MHz): δ = 1.43 [s, 6 H, C(CH_3)$_2$], 3.38 (s, 3 H, O*Me*), 3.58 [m, 4 H, (CH_2)$_2$], 6.91 (d, *J* = 7.2 Hz, 2 H, *o*-Ph), 7.05 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 7.11 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 7.26 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 7.35 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 8.26 (d, *J* = 7.8 Hz, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.6 [s, C(*C*H$_3$)$_2$], 48.5 [s, (*C*H$_2$)$_2$], 58.0 [s, *tert*-*C*(CH$_3$)$_2$], 59.1 (s, O*C*H$_3$), 73.1 [s, (*C*H$_2$)$_2$], 119.4, 121.5, 123.3, 124.4, 128.6 (overlap, *o*, *m*, *p*-*C*$_6$H$_5$), 137.3, 146.8, 158.1, 158.9 (two C_{ipso}-*C*$_6$H$_5$ and two *C*=N) ppm. $C_{20}H_{23}N_3O$ (321.42): calcd. C 74.74, H 7.21, N 13.07; found C 74.75, H 7.46, N 12.85.

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=NCH$_2$C(O)OMe(C^A–N^B)(C^B–C^C) (2): Glycine methyl ester hydrochloride (3.01 g, 24 mmol) was added to a flask containing 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (2.54 g, 8.0 mmol) and NEt_3 (4.46 mL, 32 mmol) in 40 mL of CH_2Cl_2 at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. After 14 h of stirring, the volatiles were pumped off and the residue was extracted with 30 mL of toluene to afford a pale-yellow solid. Yield: 2.45 g (92.0%). ^{1}H NMR (600 MHz): δ = 1.44 [s, 6 H, C(CH_3)$_2$], 3.77 [s, 3 H, C(=O)-OCH_3], 4.24 (s, 2 H, CH_2), 6.93 (d, *J* = 7.2 Hz, 2 H, *o*-Ph), 7.08 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 7.16 (t, *J* = 7.8 Hz, 1 H, *p*-Ph), 7.29 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 7.39 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 8.28 (d, *J* = 7.8 Hz, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.5 [s, C(*C*H$_3$)$_2$], 50.2 (s, *C*H$_2$), 52.2 [s, C(=O)O*C*H$_3$], 58.0 [s, *C*(CH$_3$)$_2$], 119.6, 121.4, 123.4, 124.7, 128.7 (overlap, *C*H-*C*$_6$H$_5$), 136.9, 146.6, 157.5, 161.1, 170.8 (two C_{ipso}-*C*$_6$H$_5$, two *C*=N, and one *C*=O) ppm. $C_{20}H_{21}N_3O_2$ (335.40): calcd. C 71.62, H 6.31, N 12.53; found C 71.52, H 6.06, N 12.44.

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=N(CH$_2$)$_2$CH$_3$(C^A–N^B)(C^B–C^C) (3): The procedure for the preparation of **3** was similar to that used for **1** but with 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (1.19 g, 3.74 mmol), NEt_3 (2.08 mL, 14.95 mmol) and propylamine (0.92 mL, 11.2 mmol). A white solid was obtained. Yield: 0.92 g (81.0%). ^{1}H NMR (600 MHz): δ = 0.98 [t, *J* = 7.2 Hz, 3 H, (CH$_2$)$_2$CH_3], 1.44 [s, 6 H, C(CH_3)$_2$], 1.65 [m, *J* = 7.2 Hz, 2 H, (CH_2)$_2$CH$_3$], 3.36 [t, *J* = 7.2 Hz, 2 H, (CH_2)$_2$CH$_3$], 6.94 (d, *J* = 7.2 Hz, 2 H, *o*-Ph), 7.06 (t, *J* = 7.8 Hz, 1 H, *p*-Ph), 7.12 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 7.28 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 7.37 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 8.30 (d, *J* = 7.8 Hz, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 11.9 [s, CH$_2$CH$_2$*C*H$_3$], 21.7 [s, C(*C*H$_3$)$_2$], 25.0 (s, CH$_2$*C*H$_2$CH$_3$), 50.4 (s, *C*H$_2$CH$_2$CH$_3$), 58.0 [s, *C*(CH$_3$)$_2$], 119.3, 121.6, 123.2, 124.2, 128.6 (overlap, *C*H-*C*$_6$H$_5$), 137.5, 147.0, 157.2, 158.3 (two C_{ipso}-*C*$_6$H$_5$ and two *C*=N) ppm. $C_{20}H_{23}N_3$ (305.42): calcd. C 78.65, H 7.59, N 13.76; found C 78.49, H 7.23, N 13.84.

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=NPh(C^A–N^B)(C^B–C^C) (4): The procedure for the preparation of **4** was similar to that used for **1** but with 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (2.07 g, 6.49 mmol), NEt_3 (3.62 mL, 26 mmol) and aniline (1.77 mL, 19.5 mmol). A pale-yellow solid was obtained. Yield: 1.98 g (89.8%). ^{1}H NMR (600 MHz): δ = 1.22 [s, 6 H, C(CH_3)$_2$], 6.92 (d, *J* = 7.2 Hz, 4 H, *o*-Ph), 7.05 (t, *J* = 7.2 Hz, 2 H, *p*-Ph), 7.19 (t, *J* = 7.5 Hz, 1 H, *p*-Ph), 7.26 (t, *J* = 7.5 Hz, 4 H, *m*-Ph), 7.41 (t, *J* = 7.8 Hz, 2 H, *m*-Ph), 8.37 (d, *J* = 7.8 Hz, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 22.4 (s, *C*H$_3$), 59.3 [s, *C*(CH$_3$)$_2$], 119.5, 121.3, 123.4, 124.8, 128.6, 128.8 (*o*, *m*, *p*-*C*$_6$H$_5$), 137.0, 146.5, 158.1 (two C_{ipso}-*C*$_6$H$_5$ and one *C*=N) ppm. $C_{23}H_{21}N_3$ (339.43): calcd. C 81.38, H 6.24, N 12.38; found C 80.88, H 6.57, N 12.43.

[{[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$OMe(C^A–N^B)(C^B–C^C)]Pd(OAc)}$_2$] (5): THF (30 mL) was added to a flask containing $Pd(OAc)_2$ (0.29 g, 1.3 mmol) and **1** (0.42 g, 1.3 mmol) at room temperature. After 10 d of stirring, the reaction mixture was filtered and the filtrate was pumped to dryness to afford a yellow solid. Yield: 0.52 g (82.2%). ^{1}H NMR (600 MHz): δ = 0.96 [s, 6 H, C(CH_3)$_2$], 1.24 [s, 6 H, C(CH_3)$_2$], 2.11 [s, 6 H, O-C(=O)-CH_3], 2.69 (m, 2 H, CH_2), 2.90 (m, 2 H, CH_2), 3.27 (s, 6 H, O*Me*), 3.55 (m, 2 H, CH_2), 3.73 (m, 2 H, CH_2), 6.90 (t, *J* = 6.6 Hz, 2 H, C*H*-Ph), 6.93 (d, *J* = 7.2 Hz, 4 H, C*H*-Ph), 7.06 (t, *J* = 7.2 Hz, 2 H, C*H*-Ph), 7.09 (t, *J* = 7.2 Hz, 2 H, C*H*-Ph), 7.28 (t, *J* = 7.8 Hz, 4 H, C*H*-Ph), 7.39 (d, *J* = 7.8 Hz, 2 H, C*H*-Ph), 8.09 (d, *J* = 7.8 Hz, 2 H, C*H*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.1 [s, C(*C*H$_3$)$_2$], 21.5 [s, C(*C*H$_3$)$_2$], 24.6 [s, O-C(=O)-*C*H$_3$], 50.4 (s, *C*H$_2$), 57.3 [s, *C*(CH$_3$)$_2$], 59.0 (s, O*C*H$_3$), 72.2 (s, *C*H$_2$), 116.2, 121.1, 123.8, 123.9, 124.6, 128.9, 134.7 (*C*H-*C*$_6$H$_5$), 120.8, 130.7, 145.8, 154.9, 159.0 (one η^1-Ph, two C_{ipso}-*C*$_6$H$_5$ and two *C*=N), 180.6 [s, O-*C*(=O)-CH$_3$] ppm. $C_{44}H_{50}N_6O_6Pd_2$ (971.74): calcd. C 54.38, H 5.19, N 8.65; found C 54.42, H 4.92, N 8.58.

[{[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=NCH$_2$C(O)OMe(C^A–N^B)-(C^B–C^C)]Pd(OAc)}$_2$] (6): THF (30 mL) was added to a flask containing $Pd(OAc)_2$ (0.67 g, 3.0 mmol) and **2** (0.91 g, 2.7 mmol) at room temperature. After 24 h of refluxing, the reaction mixture was filtered and the filtrate was pumped to dryness. The residue was washed with 15 mL of toluene to afford a reddish-brown solid. Yield: 1.22 g (90.4%). ^{1}H NMR (600 MHz): δ = 0.89 [s, 6 H, C(CH_3)$_2$], 1.20 [s, 6 H, C(CH_3)$_2$], 2.06 [s, 6 H, OC(=O)CH_3], 3.18 (d, *J* = 16.8 Hz, 2 H, CH_2), 3.60 (d, *J* = 17.4 Hz, 2 H, CH_2), 3.76

(s, 6 H, OCH_3), 6.91 (d, J = 7.8 Hz, 4 H, CH-Ph), 6.97 (t, J = 6.6 Hz, 2 H, CH-Ph), 7.07 (t, J = 7.2 Hz, 2 H, CH-Ph), 7.12 (t, J = 7.2 Hz, 2 H, CH-Ph), 7.31 (t, J = 7.8 Hz, 4 H, CH-Ph), 7.38 (d, J = 8.4 Hz, 2 H, CH-Ph), 8.05 (d, J = 7.8 Hz, 2 H, CH-Ph) ppm. $^{13}C\{^1H\}$ NMR (150 MHz): δ = 20.6 [s, C(CH_3)$_2$], 20.8 [s, C-(CH_3)$_2$], 24.3 [s, O-C(=O)-CH_3], 50.7 (s, CH_2), 52.4 [s, C(=O)-OCH_3], 57.2 [s, C(CH_3)$_2$], 116.3, 120.8, 124.2, 124.4, 124.7, 129.0, 135.0 (CH-C_6H_5), 121.2, 130.8, 145.4, 154.1, 160.1 (one η^1-Ph, two C_{ipso}-C_6H_5 and two C=N), 168.8, 181.3 [two C(=O)] ppm. $C_{44}H_{46}N_6O_8Pd_2$ (999.71): calcd. C 52.86, H 4.64, N 8.41; found C 53.43, H 4.63, N 8.17.

[{[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$CH$_3$(C^A–N^B)(C^B–C^C)]Pd(OAc)}$_2$] (7): The procedure for the preparation of **7** was similar to that used for **6** but with Pd(OAc)$_2$(1.12 g, 5 mmol) and **3** (1.37 g, 4.5 mmol). A yellow solid was obtained. Yield: 1.85 g (87.5%). ^{1}H NMR (600 MHz): δ = 0.76 [t, J = 7.2 Hz, 6 H, (CH$_2$)$_2$CH_3], 0.92 [s, 6 H, C(CH_3)$_2$], 1.20 [s, 6 H, C(CH_3)$_2$], 1.41 (m, 2 H, CH_2), 2.06 (m, 2 H, CH_2), 2.11 [s, 6 H, OC(=O)CH_3], 2.42 (m, 2 H, CH_2), 2.70 (m, 2 H, CH_2), 6.90 (t, J = 6.6 Hz, 2 H, CH-Ph), 6.93 (d, J = 7.2 Hz, 1 H, CH-Ph), 7.05 (t, J = 7.2 Hz, 2 H, CH-Ph), 7.09 (t, J = 7.2 Hz, 2 H, CH-Ph), 7.28 (t, J = 8.4 Hz, 4 H, CH-Ph), 7.42 (d, J = 8.4 Hz, 2 H, CH-Ph), 8.06 (d, J = 7.8 Hz, 2 H, CH-Ph) ppm. $^{13}C\{^1H\}$ NMR (150 MHz): δ = 11.2 [s, (CH$_2$)$_2$CH_3], 20.8 [s, C(CH_3)$_2$], 21.4 [s, C(CH_3)$_2$], 24.5 [s, O-C(=O)-CH_3], 25.2 (s, CH_2), 52.0 (s, CH_2), 57.1 [s, C(CH$_3$)$_3$], 115.9, 121.02, 123.7, 123.9, 124.5, 128.9, 135.0 (CH-C_6H_5), 120.99, 130.8, 145.9, 154.6, 157.6 (one η^1-Ph, two C_{ipso}-C_6H_5, and two C=N), 180.4 [s, O-C(=O)-CH$_3$] ppm. $C_{44}H_{50}N_6O_4Pd_2$ (939.75): calcd. C 56.24, H 5.36, N 8.94; found C 56.31, H 5.28, N 8.92.

[{[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=NPh(C^A–N^B)(C^B–C^C)]Pd(OAc)}$_2$] (8): CH$_3$CN (30 mL) was added to a flask containing Pd(OAc)$_2$ (0.45 g, 2 mmol) and **4** (0.61 g, 2 mmol) at room temperature. After 7 h of stirring, the reaction mixture was filtered and the filtrate was pumped to dryness to afford a pale-grey solid. Yield: 0.49 g (98%). ^{1}H NMR (600 MHz): δ = 0.72 [d, J = 19.8 Hz, 6 H, C(CH_3)$_2$], 1.31 [s, 3 H, O-C(=O)-CH_3], 6.95 (d, J = 7.8 Hz, 2 H, CH-Ph), 7.04 (t, J = 7.2 Hz, 1 H, CH-Ph), 7.09 (br., 3 H, CH-Ph), 7.16 (t, J = 7.8 Hz, 1 H, CH-Ph), 7.22 (m, 4 H, CH-Ph), 7.75 (d, J = 8.4 Hz, 1 H, CH-Ph), 8.26 (d, J = 7.8 Hz, 1 H, CH-Ph) ppm. $^{13}C\{^1H\}$ NMR (150 MHz): δ = 20.8, 20.0, 23.2 [one O-C(=O)-CH_3, two C(CH$_3$)$_3$], 57.9 (s, C(CH_3)$_3$), 116.0, 121.0, 124.0, 124.9, 125.5, 128.0, 128.9, 136.3 (CH-C_6H_5), 123.1, 125.5, 131.9, 142.3, 145.8, 154.9, 160.0 (one η^1-Ph, two C_{ipso}-C_6H_5 and two C=N), 180.1 [s, O-C(=O)-CH$_3$] ppm. $C_{50}H_{46}N_6O_4Pd_2$ (1007.78): calcd. C 59.59, H 4.60, N 8.34; found C 59.45, H 4.06, N 8.20.

[[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$OMe(C^A–N^B)(C^B–C^C)}PdCl] (9): Acetone (15 mL) was added to a flask containing **5** (0.27 g, 0.28 mmol) and 20 mL of saturated NaCl$_{(aq.)}$ at room temperature. After 2 h of stirring, the yellow suspension was filtered and the residue was pumped to dryness to afford a yellow solid. The crude product was washed with 20 mL of distilled water to yield a yellow solid. Yield: 0.22 g (84.3%). ^{1}H NMR (600 MHz): δ = 1.49 [s, 6 H, C(CH_3)$_2$], 3.66 (t, J = 5.1 Hz, 2 H, CH_2), 3.70 (t, J = 5.1 Hz, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 6.93 (m, 3 H, CH-Ph), 7.14 (m, 2 H, CH-Ph), 7.34 (t, J = 7.8 Hz, 2 H, CH-Ph), 8.02 (d, J = 7.8 Hz, 1 H, CH-Ph), 8.25 (br., 1 H, CH-Ph) ppm. $^{13}C\{^1H\}$ NMR (150 MHz): δ = 20.9 [s, C(CH$_3$)$_2$], 48.4 (s, CH_2), 57.0 [s, C(CH_3)$_2$], 62.3 (s, OCH$_3$), 74.3 (s, CH_2), 117.1, 120.8, 124.3, 124.7, 125.4, 129.0, 141,4 (CH-C_6H_5), 118.9, 129.9, 145.4, 153.3, 157.9 (one η^1-Ph, two C_{ipso}-C_6H_5 and two C=N) ppm. $C_{20}H_{22}ClN_3OPd$ (462.28): calcd. C 51.96, H 4.80, N 9.09; found C 51.92, H 4.83, N 8.60.

[{PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=NCH$_2$C(O)OMe(C^A–N^B)-(C^B–C^C)}PdCl] (10): The procedure for the preparation of **10** was similar to that used for **9** but with **6** (0.72 g, 0.74 mmol), 20 mL of saturated NaCl$_{(aq.)}$ and 15 mL of acetone. A yellow solid was obtained. Yield: 0.48 g (68.6%). ^{1}H NMR [600 MHz, (CD$_3$)$_2$SO]: δ = 1.38 [s, 6 H, C(CH_3)$_2$], 3.72 (s, 3 H, OCH_3), 4.31 (s, 2 H, CH_2), 6.80 (m, 1 H), 7.02 (m, 3 H), 7.14 (t, J = 7.5 Hz, 1 H, CH-Ph), 7.36 (t, J = 7.8 Hz, 2 H, CH-Ph), 7.91 (d, J = 7.2 Hz, 1 H, CH-Ph), 7.93 (d, J = 7.8 Hz, 1 H, CH-Ph) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, (CD$_3$)$_2$SO): δ = 20.2 [s, C(CH$_3$)$_2$], 49.7 (s, CH_2), 52.2 (s, OCH$_3$), 115.5, 120.8, 123.4, 124.0, 124.3, 128.9, 140,9 (CH-C_6H_5), 118.5, 130.9, 145.4, 154.2, 160.8, 170.5 [one C(=O), one η^1-Ph, two C_{ipso}-C_6H_5 and two C=N] ppm. $C_{20}H_{20}ClN_3O_2Pd$ (476.26): calcd. C 50.44, H 4.23, N 8.82; found C 50.20, H 4.35, N 8.59.

[{[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$CH$_3$(C^A–N^B)(C^B–C^C)]PdCl}$_2$] (11): The procedure for the preparation of **11** was similar to that used for **9** but with **4** (0.12 g, 0.13 mmol), 20 mL of saturated NaCl$_{(aq.)}$ and 15 mL of acetone . A yellow solid was obtained. Yield: 0.10 g (90.5%). ^{1}H NMR (600 MHz): δ = 0.83 [s, 3 H, CH$_2$CH_3], 1.38 [d, J = 9 Hz, 6 H, C(CH_3)$_2$], 1.78 [m, 2 H, (CH_2)$_2$CH$_3$], 3.43 [m, 3 H, (CH_2)$_2$CH$_3$], 6.87 (d, J = 8.4 Hz, 2 H, CH-Ph), 7.05 (m, 2 H, CH-Ph), 7.25 (t, J = 7.8 Hz, 2 H, CH-Ph), 7.51 (t, J = 8.4 Hz, 1 H, CH-Ph), 7.90 (d, J = 7.8 Hz, 1 H, CH-Ph) ppm. $^{13}C\{^1H\}$ NMR (150 MHz): δ = 11.1 [s, (CH$_2$)$_2$CH_3], 21.4 [s, C(CH_3)$_2$], 25.5 [s, (CH_2)$_2$CH$_3$], 52.9 [s, (CH_2)$_2$CH$_3$], 57.0 [s, C(CH$_3$)$_2$], 116.0, 120.9, 124.0, 124.5, 125.2, 128.9, 138.0 (CH-C_6H_5), 120.5, 130.1, 145.7, 153.7, 158.5 (one η^1-Ph, two C_{ipso}-C_6H_5 and two C=N) ppm. $C_{40}H_{44}Cl_2N_6Pd_2$ (892.56): calcd. C 53.83, H 4.97, N 9.42; found C 53.94, H 5.25, N 9.34. HRMS: m/z for $C_{40}H_{44}Cl_2N_6Pd_2$ (M^+): calcd. 890.1074; found 890.1071.

General Procedure for the Suzuki Reaction: The appropriate amounts of catalyst, base (2.0 equiv.), boronic acid (1.5 equiv.) and aryl halide (1.0 equiv.) were placed in a Schlenk tube under nitrogen. Solvent (2 mL) was added by syringe, and the reaction mixture was stirred at room temperature or heated to the appropriate temperature for the appropriate time.

General Procedure for the Heck-type Reaction: The appropriate amounts of catalyst, base (1.5 equiv.) and aryl halide (1 equiv., solids) were placed in a Schlenk tube under nitrogen. Solvent (2 mL), styrene (1.3 equiv.) and aryl halides (1 equiv., liquids) were added by syringe, and the reaction mixture was heated to the appropriate temperature for the appropriate time.

Crystal Structure Data: Crystals were grown from concentrated hexane solution (**2** and **4**), CH$_2$Cl$_2$/hexane solution (for **5**, **7** and **8**) or chloroform solution (for **9**) and isolated by filtration. They 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.[26] 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 was solved by direct methods using the SHELXTL package.[27] 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 3.

CCDC-678688 (for **2**), -678689 (for **4**), -678690 (for **5**), -678691 (for **7**), -678692 (for **8**) and -678693 (for **9**) contain the supplementary

Table 3. Summary of crystal data for compounds **2**, **4**, **5**, **7**, **8** and **9**.

	2	**4**	**5**·2CH_2Cl_2·H_2O	**7**·0.5CH_2Cl_2	**8**·CH_2Cl_2	**9**
Formula	$C_{20}H_{21}N_3O_2$	$C_{23}H_{21}N_3$	$C_{46}H_{50}Cl_4N_6O_7Pd_2$	$C_{89}H_{100}Cl_2N_{12}O_8Pd_4$	$C_{51}H_{48}Cl_2N_6O_4Pd_2$	$C_{20}H_{22}ClN_3OPd$
Fw	335.40	339.43	1153.52	1962.31	1092.65	462.26
T [K]	297(2)	297(2)	297(2)	297(2)	297(2)	297(2)
Crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	9.002(2)	9.1696(11)	15.408(3)	11.1482(9)	11.461(3)	11.1268(15)
b [Å]	9.664(2)	11.3274(14)	20.769(5)	12.3221(11)	12.590(3)	15.317(2)
c [Å]	11.257(3)	11.4899(13)	18.664(4)	18.0280(15)	18.745(4)	12.7024(17)
α°	82.840(5)	60.765(2	90	70.409(2)	106.822(4)	90
β [°]	72.492(5)	76.296(2)	113.175(4)	72.549(2)	103.947(5)	115.158(2)
γ [°]	75.453(5)	67.895(2)	90	83.226(2)	97.723(5)	90
V [Å^3]	902.7(4)	962.8(2)	5491(2)	2225.3(3)	2451.3(10)	1959.4(5)
Z	2	2	4	1	2	4
$\rho_{calcd.}$ [Mg/m^3]	1.234	1.171	1.395	1.464	1.480	1.567
μ(Mo-K_α) [mm]$^{-1}$	0.081	0.070	0.899	0.916	0.893	1.097
Reflections collected	5165	5551	15378	25290	13934	10892
No. of parameters	226	235	316	527	586	235
$R1$[a]	0.0628	0.0607	0.0419	0.0354	0.0406	0.0339
wR_2[a]	0.1535	0.1594	0.1236	0.1293	0.0928	0.1030
GoF [b]	1.017	1.015	1.005	1.035	1.036	1.019

[a] $R1 = [\Sigma(|F_o| - |F_c|)/\Sigma |F_o|]$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 0.10$. [b] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

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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