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# Synthesis and Structural Characterization of Palladacycles with Polydentate Ligands by a Stepwise Coupling Route – Palladacycles Containing Halides as Efficient Catalysts and Substrates

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**Keywords:** Palladium / Sandwich complexes / Homogeneous catalysis / Amination / Halides / Palladacycles

A series of ferrocenyl palladacycles with polydentate ligands were conveniently prepared by the Suzuki coupling reactions of a halide-containing ferrocenyl palladacycle [PdCl({($\eta^5$-$C_5H_5$)}Fe{($\eta^5$-$C_5H_3$)$N_2C_4H_2$Cl})($PPh_3$)] (**1**) and arylboronic acids without additional palladium catalysis. In the absence of additional base, amination also occurred in high yield. This new protocol was successfully applied to the Suzuki coupling reactions of the analogous halide-containing palladacycle [PdCl({($\eta^5$-$C_5H_5$)}Fe{($\eta^5$-$C_5H_3$)$NC_5H_3$Br})($PPh_3$)] (**15**) and Buchwald–Hartwig amination of the analogous complex [PdCl({($\eta^5$-$C_5H_5$)}Fe{($\eta^5$-$C_5H_3$)$NC_5H_3$Br})(DCPAB)] (**32**), where DCPAB = 2-dicyclohexylphosphanyl-2′-(*N*,*N*-dimethylamino)biphenyl. The halide-containing palladacycles act as efficient catalysts and substrates in the coupling reactions. 37 new examples have been fully characterized by elemental analysis, IR and $^1$H NMR spectroscopy, and ESI-MS. Additionally, the molecular structures of eight compounds were determined by single-crystal X-ray diffraction, and many types of intermolecular C–H···Cl (O, N, π) interactions and π–π interactions were found in the crystal structures of these palladacycles.

## Introduction

Palladium-catalyzed coupling reactions, such as the Suzuki coupling reaction and the Buchwald–Hartwig amination, have become powerful methods in organic synthesis.[1] A number of Pd catalyst precursors, usually simple palladium salts or complexes associated with the appropriate ligands, can mediate these reactions under various reaction conditions. Among them, palladacycles are one of the most developed and studied classes of precatalyst because of their structural versatility and high catalytic activity.[2] Since the first report on the use of palladacycles for coupling reactions by Herrmann in 1995,[3] a wide variety of palladacycles have been successfully used in these reactions. For instance, monophosphane palladacycles combine the stability imparted by a palladacycle framework with the high activity commonly associated with monophosphane ligands and are far more active than the corresponding dimeric palladacycles.[4] In particular, cyclopalladated ferrocene derivatives are fascinating as ferrocene is an ideal framework to which planar chirality can be introduced.[5] Various methods for the preparation of these complexes have been developed, and they can be mainly divided into four strategies: C–H activation, oxidative addition, transmetalation, and nucleophilic addition.[2c] C–H activation is the simplest and most direct process (Scheme 1, **A**), however, a synthetic limitation has emerged as a serious problem. First, cyclopalladated complexes with free donor groups may be difficult to prepare by cyclopalladation because the precursor polydentate ligand may coordinate to the Pd center and block C–H activation.[6] Furthermore, in the direct cyclopalladation protocol by C–H activation, the regioselectivity of cyclopalladation is not controlled. To overcome these problems, we planned to develop a stepwise coupling route (stepwise introduction of the free donor groups) for the synthesis of palladacycles with polydentate ligands (Scheme 1, **B**). These complexes can be used as metalloligands for the synthesis of cyclopalladated polynuclear complexes.

Palladium-catalyzed coupling reactions of cyclometalated halide-containing iridium complexes with arylboronic acids have been reported.[7] To the best of our knowledge, there are no reports concerning the coupling reactions of halide-containing palladacycles. In recent years, part of our research effort has focused on the synthesis and application of cyclometalated complexes.[8] In a preliminary communication,[9] we reported a new triphenylphosphane cyclopalladated ferrocenylchloropyrimidine complex **1**, which reacted with KOH to provide a $Pd_4$ cluster monophosphane palladacycle by Pd-catalyzed hydroxylation. In view of these findings and our continued

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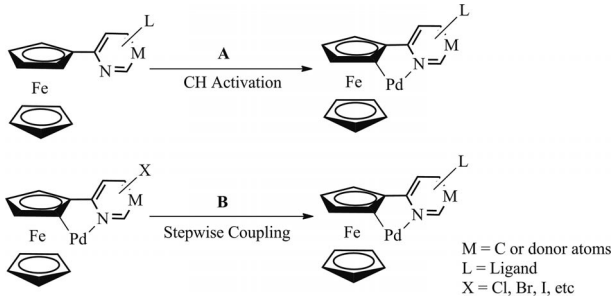


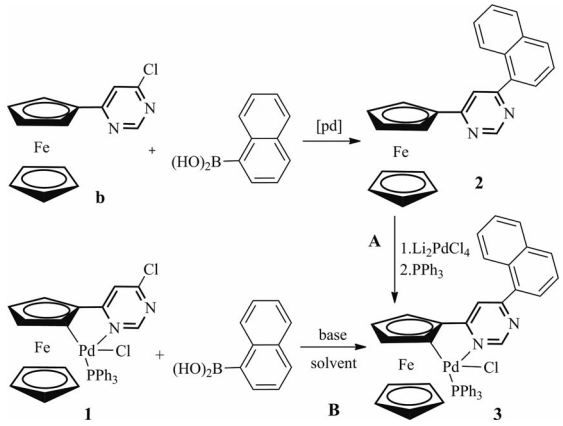

Scheme 1. Synthetic strategy for palladacycles with polydentate ligands.

interest in other coupling reactions of **1** and analogous halide-containing palladacycles, we examined their role and catalytic activity in Suzuki and C–N coupling reactions. Here, we present an efficient method for the synthesis of palladacycles with polydentate ligands by a stepwise coupling route and the synthesis and structural characterization of these palladacycles.

## Results and Discussion

### Synthesis of Palladacycles with Polydentate Ligands by Stepwise Suzuki Coupling Reactions

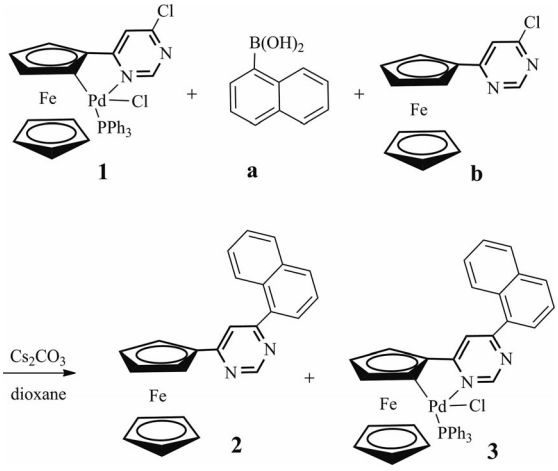
There are two pathways for the synthesis of palladacycles with a polydentate ligand (Scheme 2, **A** and **B**). According to the traditional method (**A**), **3** was obtained from Suzuki coupling, cyclopalladation, and bridge-splitting reactions. Considering that **1** is a chloride-containing (in the pyrimidine ring) monophosphane palladacycle, we speculate that it reacted with arylboronic acids both as catalyst and substrate. The new pathway **B** is contrary to route **A** in sequence, which is particularly attractive because it does not require an additional palladium catalyst. If it can be successfully applied to the coupling reactions, other ligands could be introduced to the cyclopalladated ligand. This strategy enabled us to prepare a new class of palladacycles with polydentate ligands.




Scheme 2. Synthesis of **3**.

In order to further examine the role and catalytic activity of **1** in the coupling reaction and to develop a new stepwise synthetic strategy, we researched the Suzuki coupling of **1** with naphthylboronic acid (Scheme 2, **B**). Based on our previous experiments on palladacylic precatalysts for Suzuki coupling reactions,[4c,10] the reaction was performed under a nitrogen atmosphere in dioxane in the presence of $Cs_2CO_3$ at 110 °C for 16 h, which afforded the coupled product **3** in 93% yield (Table 1, Entry 1) without an additional palladium catalyst. Other reaction conditions such as $K_2CO_3$ in dioxane, $K_3PO_4$ in dioxane, $K_2CO_3$ in toluene, and $K_3PO_4$ in toluene afforded good yields (91, 85, 89, and 83%, respectively).

Table 1. Effect of **1** on Suzuki coupling reactions.[a]



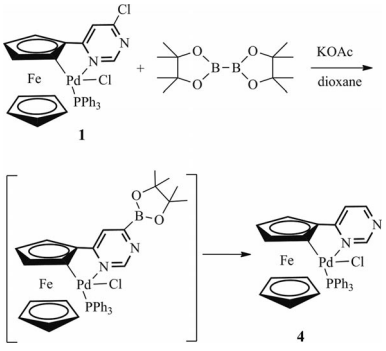

| Entry | Equiv. **1** | Equiv. **a** | Equiv. **b** | % Yield of **2**[b] | % Yield of **3**[b] |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 0 | 0 | 93 |
| 2 | 0.1 | 1 | 1 | 88 | 85 |
| 3 | 0.5 | 1 | 1 | 39 | 87 |
| 4 | 1 | 1 | 1 | 0 | 90 |
| 5 | 0.01 | 1 | 1 | 73 | trace |
| 6 | 0.001 | 1 | 1 | 18 | trace |
| 7 | 1 | 4 | 1 | 90 | 92 |
| 8 | 1 | 5 | 0 | 0 | 95 |

[a] Reaction conditions: **b** (0.5 mmol), $Cs_2CO_3$ (1.0 mmol), dioxane (5 mL), 110 °C, 16 h. [b] Isolated yield.

We next explored the effect of **1** on Suzuki coupling reactions. Employing a mixture of **1**, **a**, and **b**, the coupled product **3** was obtained in good yields (Table 1, Entries 2–4). However, the product **2** was not isolated using 1.0 equiv. of **1** (Entry 4). Furthermore, **1** could be present in lower than 1 mol-% without loss of activity (Entry 5), however, the yield of **2** only reached 18% when 0.1 mol-% of **1** was used (Entry 6), which revealed that a small percentage (less than 0.1 mol-%) of **1** behaves as the catalyst[11] and the remaining **1** behaves as the substrate. The results indicated that **1** was an efficient precatalyst.[10c] Loading naphthylboronic acid (**a**) to 4.0 equiv. gave **2** and **3** in 90–92% yields, respectively (Entry 7). Although the reductive ring-opening reactions of palladacyclic catalysts have been reported in the couplings of arylboronic acids with palladacycles,[12] **2** was not obtained with 5.0 equiv. of **a** in this reaction (Entry 8).

Additionally, we also investigated the coupling reaction of **1** with bis(pinacolato)diboron (Scheme 3). Although, palladium-catalyzed coupling reactions of bis(pinacolato)-diboron with aryl halides have been extensively studied,[13] to the best of our knowledge, there are no reports concerning the coupling reactions of halide-containing palladacycles with bis(pinacolato)diboron. The reaction gave **4** in moderate yield (52%) and its molecular structure is shown in Figure S1–S2 (see Supporting Information). The corresponding boronate was not observed; a possible reason was that the *ortho*-substituted pinacol ester of pyrimidinylboronic acid formed was not stable under the reaction conditions.[14] The results also indicated that **1** was a efficient catalyst precursor and substrate in reaction.

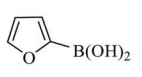
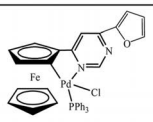
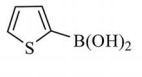
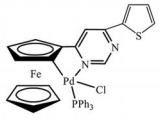
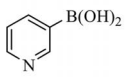
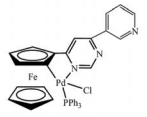
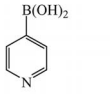
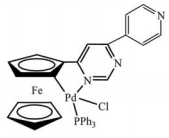
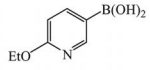
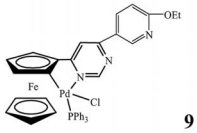
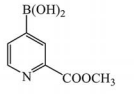
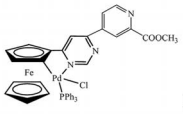
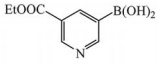
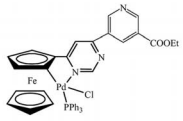
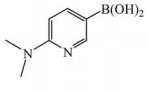
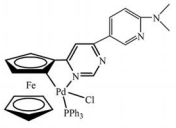
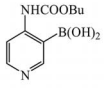
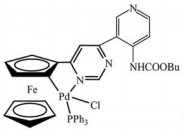



Scheme 3. Reaction of bis(pinacolato)diboron and **1**.

In contrast to arylboronic acids, Suzuki coupling reactions of heteroarylboronic acids have been less reported.[15] To obtain palladacycles containing more free donor groups, the Suzuki coupling reactions of a variety of structurally diverse heteroarylboronic acids with **1** were investigated in the presence of $K_2CO_3$ ($Cs_2CO_3$ is more expensive than $K_2CO_3$) in dioxane. The corresponding palladacycles were isolated in good yields (86–92%) for heteroarylboronic acids such as 2-furylboronic acid, thiophen-2-boronic acid, and pyridinylboronic acid (Table 2, Entries 1–4). Next, we proceeded to examine the substrate scopes with respect to pyridinylboronic acids. The method proved to be effective for pyridinylboronic acids bearing a variety of functional groups, including ethers (Entry 5), esters (Entries 6–7) and amines (Entry 8). However, for the very sterically hindered pyridinylboronic acid, the corresponding palladacycle was obtained in low yield (Entry 9).

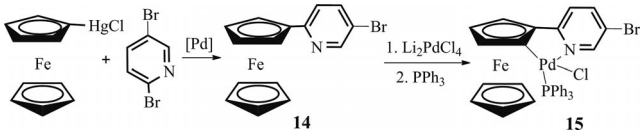
In order to extend the scope of this catalyst system to other halide-containing palladacycles, we synthesized the analogous **15** according to reported procedures (Scheme 4).[4d,9] The newly developed Suzuki reaction protocol was also successfully applied to heteroarylboronic acids and **15**. As shown in (Table 3), a series of heteroarylboronic acids were efficiently transformed to the desired products in good yields (Entries 1–6). Compared with those starting from **1**, the yields of coupled products starting from **15** decreased slightly. This may be because the activity of the bromine atom in **15** is lower than that of the chlorine atom in **1**.

Table 2. Suzuki coupling reactions of heteroaryl–$B(OH)_2$ with **1**.[a]

| Entry | Heteroaryl-$B(OH)_2$ | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  **5** | 92 |
| 2 |  |  **6** | 90 |
| 3 |  |  **7** | 88 |
| 4 |  |  **8** | 89 |
| 5 |  |  **9** | 87 |
| 6 |  |  **10** | 90 |
| 7 |  |  **11** | 86 |
| 8 |  |  **12** | 92 |
| 9 |  |  **13** | 41 |

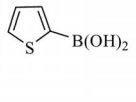
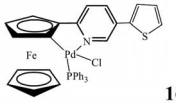
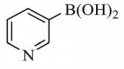
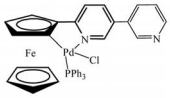
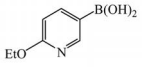
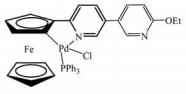
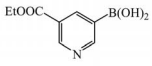
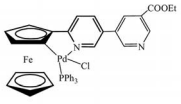
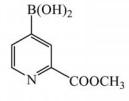
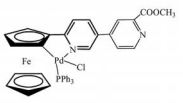
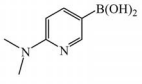
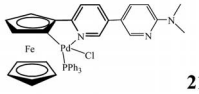
[a] Reaction conditions: **1** (0.5 mmol), heteroaryl–$B(OH)_2$ (0.6 mmol), $K_2CO_3$ (1.0 mmol), dioxane (5 mL), 110 °C, 24 h. [b] Isolated yield.



Scheme 4. Synthesis of **14** and **15**.

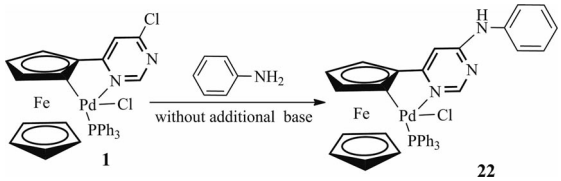
Table 3. Suzuki coupling reactions of heteroaryl–$B(OH)_2$ with **15**.[a]

| Entry | Heteroaryl-$B(OH)_2$ | Product | Yield [%][b] |
|---|---|---|---|
| 1 |  |  **16** | 89 |
| 2 |  |  **17** | 87 |
| 3 |  |  **18** | 90 |
| 4 |  |  **19** | 86 |
| 5 |  |  **20** | 92 |
| 6 |  |  **21** | 90 |

[a] Reaction conditions: **15** (0.5 mmol), heteroaryl–$B(OH)_2$ (0.6 mmol), $K_2CO_3$ (1.0 mmol), dioxane (5 mL), 110 °C, 24 h. [b] Isolated yield.

## Synthesis of Palladacycles with Polydentate Ligands by Stepwise C–N Coupling Reactions

The high activity of **1** in the Suzuki coupling reactions of arylboronic acids encouraged us to examine their activity towards C–N coupling reactions. It is known that the catalyst and base are crucial components of the Buchwald–Hartwig amination.[16] Beller reported transition metal-free amination of aryl chlorides, which proceed efficiently in the presence of an excess of KO*t*Bu.[17] We have also found that cyclopalladated complexes are very efficient for the amination of aryl chlorides in the presence of KO*t*Bu or KOH as a base.[4d,4e] Considering that **1** is a chloride-containing palladacycle, it can react with KOH to provide a hydroxy product.[9] Thus, we chose the coupling of aniline with **1** as the model reaction to evaluate the effectiveness of **1** in dioxane without additional base (Scheme 5), and the desired product **22** was obtained in good yield (88%). When $K_2CO_3$ was used as the base, the yield increased slightly to 91%. However, the hydroxy product was not observed in the reaction. Other solvents such as toluene also afforded good yield (85%).



Scheme 5. Synthesis of **22**.

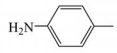
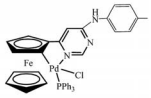
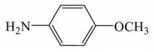
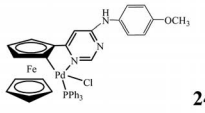
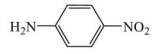
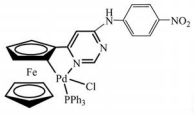
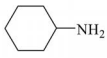
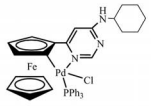
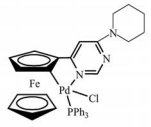
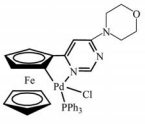
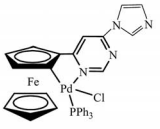
A variety of electronically and structurally diverse amines could be coupled efficiently with **1** in the absence of additional base in dioxane at 110 °C for 24 h (Table 4). Similar to the results with aniline, the reactions of *p*-toluidine and 4-methoxyaniline with **1** provided high isolated yields (Entries 1–2). However, for 4-nitroaniline only 30% isolated yield was obtained under the same conditions (Entry 3). The reactions of primary aliphatic amines of aryl chlorides are not common in amination reactions. We also examined the aminations of aliphatic amines with **1**, and, unexpectedly, the yields of aliphatic amines (90–95%) are better than the yield of aniline in most cases (Entries 4–6). In order to introduce more free donor groups to the palladacycles, we investigated the amination of imidazole with **1** (Entry 7), and the corresponding product was isolated in good yield (91%).

To further explore the role of **1** in the above coupling reactions, we performed the parallel coupling reaction of **b** and aniline (Scheme 6). The coupled product **30** was also obtained in moderate yield (53%) in the absence of additional base. However, the corresponding product was not obtained by the reaction of **14** with aniline (Table 5, Entry 1). The result revealed that **1** could only act as a substrate in the reaction. The C–N bond formation in **22** is due to the strong activity of the chloride atom (in the pyrimidine ring).[18] Even when the strong organic base KO*t*Bu was used, the coupling of the analogous halide-containing palladacycle **15** and aniline was also unsuccessful (Entry 2), indicating that **1** and **15** are inactive in Buchwald–Hartwig aminations.

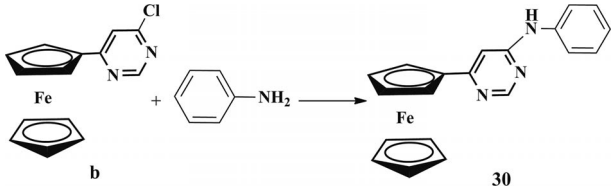
Based on our previous experiments on palladacylic precatalysts for Buchwald–Hartwig aminations,[4d,4e] we performed the aminations of **14** or **15** and aniline catalyzed by **31**[4e] (Figure 1). As expected, the corresponding products were obtained in good yields (Entries 3–4). To explore the "real" catalyst in the reaction, **32** was also synthesized. Subsequent experiments further proved that **32** was an efficient catalyst precursor for Buchwald–Hartwig aminations (Entries 5–6) suggesting that DCPAB participated in the catalytic cycle. On the basis of these results, we propose that

Table 4. C–N coupling reactions of various amines with **1**.[a]

| Entry | Amine | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  **23** | 89 |
| 2 |  |  **24** | 91 |
| 3 |  |  **25** | 30 |
| 4 |  |  **26** | 92 |
| 5 |  |  **27** | 95 |
| 6 |  |  **28** | 93 |
| 7 |  |  **29** | 91 |

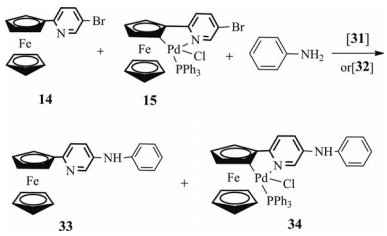
[a] Reaction conditions: **1** (0.5 mmol), amine (0.75 mmol), dioxane (5 mL), 110 °C, 24 h. [b] Isolated yield.



Scheme 6. Synthesis of **30**.

the phosphane ligand may promote the release of the real catalytic species from the palladacycle, and stabilize the active species under the reaction conditions. It is proposed

Table 5. Effect of **31** or **32** on Buchwald–Hartwig aminations.[a]



| Entry | Equiv. **14** | Equiv. **15** | Equiv. aniline | Equiv. catalyst | % Yield[b] |
|---|---|---|---|---|---|
| 1 | 1 | 0 | 1.5 | 0 | **33** (0) |
| 2 | 0 | 1 | 1.5 | 0 | **34** (0) |
| 3 | 1 | 0 | 1.5 | **31** (0.001) | **33** (91) |
| 4 | 0 | 1 | 1.5 | **31** (0.001) | **34** (94) |
| 5 | 1 | 0 | 1.5 | **32** (0.001) | **33** (90) |
| 6 | 0 | 1 | 1.5 | **32** (0.001) | **34** (92) |

[a] Reaction conditions: **14** (0.5 mmol) or **15** (0.5 mmol), aniline (0.75 mmol), KO*t*Bu (1.0 mmol), dioxane (5 mL), 110 °C, 24 h. [b] Isolated yield.

that the coupling reaction catalyzed by small percentage of halide-containing palladacycle proceeded through a classical $Pd^0/Pd^{II}$ cycle.[11,19]

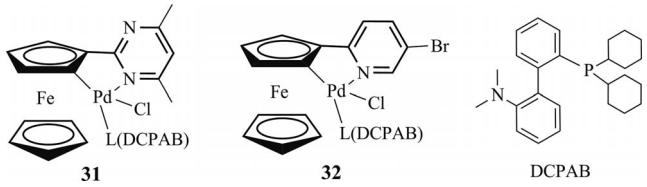


Figure 1. Ferrocenyl palladacycles **31** and **32**.

Finally, this newly developed coupling protocol was also successfully applied to the synthesis of palladacycles with polydentate ligands by Buchwald–Hartwig aminations of **32**. As shown in Table 6, **32** was very effective in the arylation of aniline and 4-methoxyaniline (Entries 1–2). However, the yields of aliphatic amines in this system decreased slightly (Entries 3–4). For imidazole, the corresponding product was isolated in good yield (Entry 5).

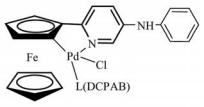
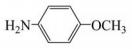
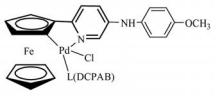
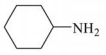
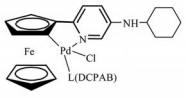
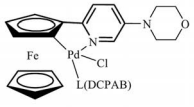
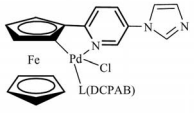
## Crystal Structures and Intermolecular Interactions

Although many structures of palladacycles have been determined, few reports discuss the intermolecular interactions in these complexes.[20] We systematically investigated the crystal structures of palladacycles **3**, **10**, **11**, **15**, **17**, **26**, **27**, and **32**, focusing on their supramolecular interactions.

All the crystals were obtained by recrystallization from $CH_2Cl_2$/petroleum ether solution at room temperature. The single-crystal X-ray analysis indicates that these palladacycles are *trans* complexes in the solid state. The Pd atom in each complex is in a slightly distorted square planar environment bonded to the phosphorus, chloride, pyrimidinyl nitrogen, and a carbon atom of the ferrocenyl moiety.

Table 6. Buchwald–Hartwig aminations of various amines with **32**.[a]

| Entry | Amine | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  **35** | 90 |
| 2 |  |  **36** | 92 |
| 3 |  |  **37** | 82 |
| 4 |  |  **38** | 80 |
| 5 |  |  **39** | 95 |

[a] Reaction conditions: **32** (0.5 mmol), amines (0.75 mmol), KO*t*Bu (1.0 mmol), dioxane (5 mL), 110 °C, 24 h. [b] Isolated yield.

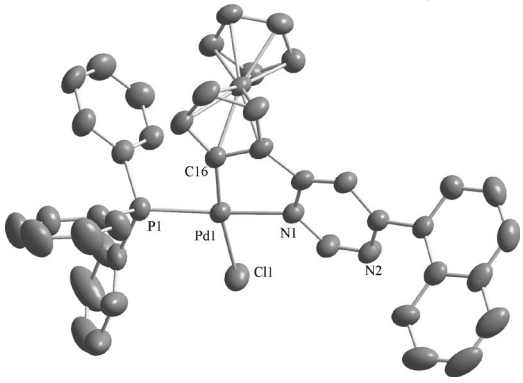



Figure 2. Molecular structure of **3**·2$CH_2Cl_2$. Thermal ellipsoids are drawn at 50% probability. H atoms and $CH_2Cl_2$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(16) 1.999(5), Pd(1)–N(1) 2.130(4), Pd(1)–P(1) 2.2402(14), Pd(1)–Cl(1) 2.3842(15) and C(16)–Pd(1)–N(1) 80.80(18), C(16)–Pd(1)–P(1) 92.11(15), P(1)–Pd(1)–Cl(1) 95.30(5), N(1)–Pd(1)–Cl(1) 91.93(12).

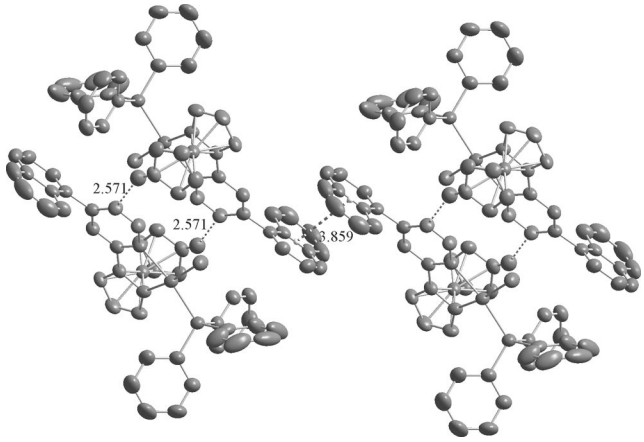



Figure 3. 1D chain structure of **3**·2$CH_2Cl_2$ showing the C–H···N hydrogen bonds and π–π interactions. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms and $CH_2Cl_2$ are omitted for clarity.

The molecular structure of **3** is shown in Figure 2. The bicyclic system formed by the palladacycle and the $C_5H_3$ moiety is approximately coplanar (dihedral angles of 1.1°). However, the pyrimidine and naphthalene rings are not coplanar and have a dihedral angle of 50.7°. In **3**·2$CH_2Cl_2$, there are C–H···N hydrogen bonds and π–π stacking interactions between the naphthalene rings,[21] which are attributed to the 1D chain structure (Figure 3). In addition, $CH_2Cl_2$ molecules are present in the two adjacent chains and form intermolecular C–H···Cl hydrogen bonds (Cl···H 2.895 Å) with the chlorine atom of **3** (Figure S3–S4, Supporting Information).

Hydrogen bonds are considered to be the most powerful organizing element in molecular assembly due to their highly selective and directional character. In particular, C–H···Cl hydrogen bonds have attracted great interest as the H-bonding acceptor capability of terminal metal-bound chlorine (M–Cl) is stronger than their C–Cl analogues in organometallic compounds.[22] Therefore, C–H···Cl–M hydrogen bonding can be used to assemble transition metal-based building blocks into supramolecular structures.[23] The molecular structures of **10** and **11** were confirmed by single-crystal X-ray diffraction analysis (see Figures 4, 5, and Figure S5 in the Supporting Information). The crystal structures of the two complexes are similar, the oxygen atom of ester group forms C–H···O hydrogen bonds, however, the nitrogen atom in the pyridine ring does not participate in hydrogen bonding. In comparison with **3**·2$CH_2Cl_2$, the chlorine atom of **10** forms three types of intermolecular C–H···Cl hydrogen bonds with adjacent C–H groups of the Cp and pyridine rings, which give rise to a 1D chain (Figure 4). Like **10**, **11** also has a 1D chain structure formed by C–H···Cl and C–H···O(ester) hydrogen bonds (Figure S6, Supporting Information). It is noteworthy that intermolecular π–π interactions involving the neighboring pyridine rings (the interplanar distance is 3.659 Å) are also present

in **11**. Owing to the π–π stacking effects and C–H···Cl(O) hydrogen bonds, the crystal structure of **11** is extended into a 2D architecture (Figure 6).

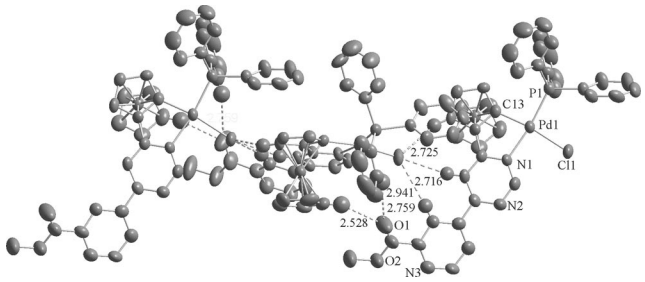



Figure 4. 1D chain structure of **10** showing the C–H···Cl(O) hydrogen bonds. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(13) 1.994(7), Pd(1)–N(1) 2.127(6), Pd(1)–P(1) 2.242(2), Pd(1)–Cl(1) 2.379(2) and C(13)–Pd(1)–N(1) 80.8(3), C(13)–Pd(1)–P(1) 92.3(2), P(1)–Pd(1)–Cl(1) 95.90(8), N(1)–Pd(1)–Cl(1) 91.79(17).

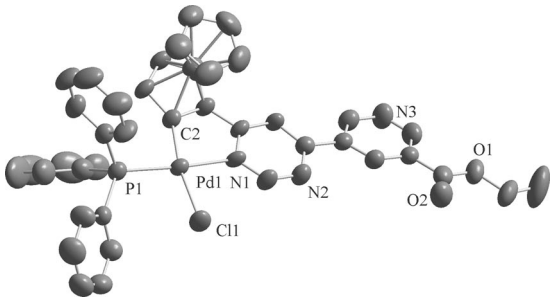



Figure 5. Molecular structure of **11** (one of the two independent molecules). Thermal ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (corresponding values for the second independent molecule are given in brackets): Pd(1)–C(2) 1.983(4) [1.981(4)], Pd(1)–N(1) 2.127(3) [2.131(3)], Pd(1)–P(1) 2.2442(13) [2.2235(13)], Pd(1)–Cl(1) 2.3740(12) [2.3856(12)] and C(2)–Pd(1)–N(1) 80.70 (15) [81.02(15)], C(2)–Pd(1)–P(1) 92.28(13) [90.57(13)], P(1)–Pd(1)–Cl(1) 97.01(5) [95.67(4)], N(1)–Pd(1)–Cl(1) 90.28(10) [94.54(10)].

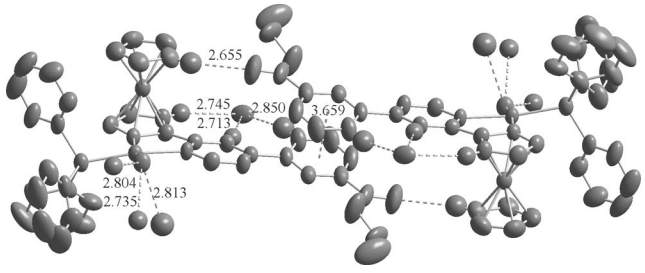



Figure 6. Two-dimensional lamellar structure of **11** showing the C–H···Cl(O) hydrogen bonds and π–π interactions. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity.

The molecular structure of **15** is shown in Figure S7 (Supporting Information). It can be seen from Figure 7 that **15** also has a 1D chain structure formed by C–H···Cl hydrogen bonds, whereas the bromine atom on the pyridine ring does not participate in hydrogen bonding. In complex **17** (Figure 8), there are two types of C–H···Cl hydrogen bonds and C–H···N interactions, which are attributed to the 1D chain structure. Interestingly, the uncoordinated pyridinyl nitrogen atom also forms intermolecular C–H···N hydrogen bonds with the adjacent C–H group of the Cp ring, which is not found in the structures of **10** and **11**. In addition, $CH_2Cl_2$ molecules are present in the two adjacent chains (Figure 9).

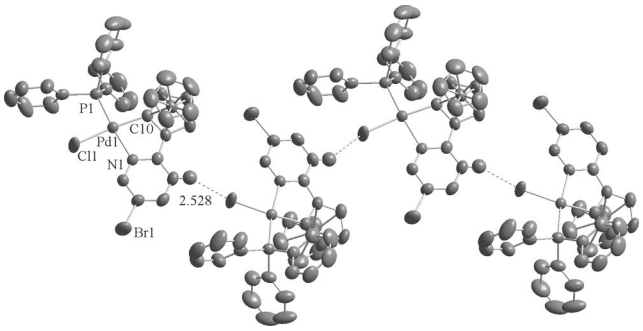



Figure 7. 1D chain structure of **15** showing the C–H···Cl hydrogen bonds. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(10) 1.988(4), Pd(1)–N(1) 2.140(3), Pd(1)–P(1) 2.2322(11), Pd(1)–Cl(1) 2.3642(2) and C(10)–Pd(1)–N(1) 81.38(15), C(10)–Pd(1)–P(1) 90.34(12), P(1)–Pd(1)–Cl(1) 94.81(4), N(1)–Pd(1)–Cl(1) 91.80(9).

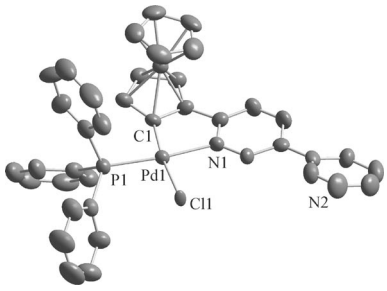



Figure 8. Molecular structure of **17** (one of the two independent molecules). Thermal ellipsoids are drawn at 50% probability. H atoms and $CH_2Cl_2$ are omitted for clarity. Selected bond lengths [Å] and angles [°] (corresponding values for the second independent molecule are given in brackets): Pd(1)–C(1) 1.990(7) [1.992(7)], Pd(1)–N(1) 2.150(5) [2.141(5)], Pd(1)–P(1) 2.2454(18) [2.2398(17)], Pd(1)–Cl(1) 2.4713(13) [2.4213(14)] and C(1)–Pd(1)–N(1) 80.9(2) [80.9(3)], C(2)–Pd(1)–P(1) 92.3(2) [92.0(2)], P(1)–Pd(1)–Cl(1) 93.80(6) [94.58(6)], N(1)–Pd(1)–Cl(1) 93.06(15) [93.64(15)].

Figure 10 shows that **26** exists as a dimer due to intermolecular N–H···N hydrogen bonds and the chlorine atom that forms a hydrogen bond with the adjacent C–H group of $CH_2Cl_2$. This is different from the structures of **10**, **11**, **15**, and **17**, which have 1D chain structures formed by C–H···Cl hydrogen bonds. The molecular structure of **27** is shown in Figure 11. Unlike **26**, **27** also has a 1D chain structure formed by C–H···Cl hydrogen bonds. It is worth noting that the intermolecular C–H···π interactions[20d,24] are present in **27**, resulting in a 2D supramolecular architecture (Figure 12).

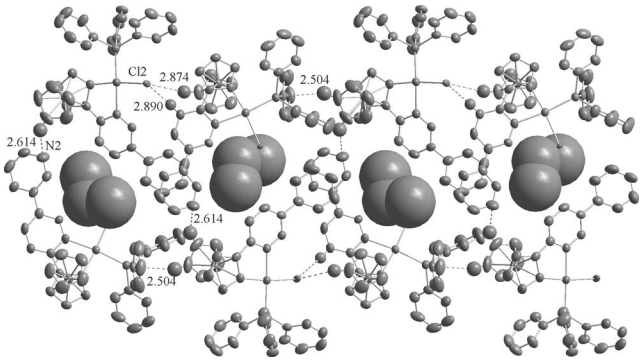



Figure 9. 2D lamellar structure of **17** showing the C–H···Cl(N) interactions. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity.

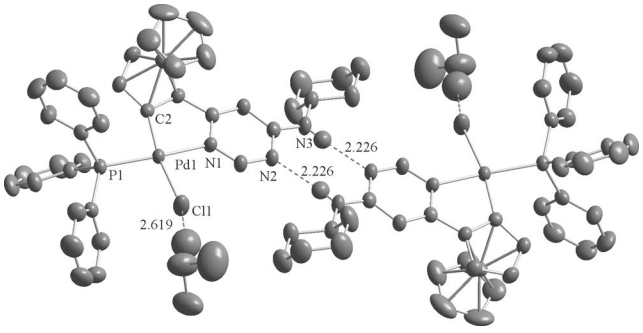



Figure 10. The dimeric structure of **26** showing the C–H···N hydrogen bonds. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(2) 1.991(3), Pd(1)–N(1) 2.118(2), Pd(1)–P(1) 2.2407(8), Pd(1)–Cl(1) 2.3818(9) and C(2)–Pd(1)–N(1) 80.63(11), C(2)–Pd(1)–P(1) 92.75(9), P(1)–Pd(1)–Cl(1) 95.56(3), N(1)–Pd(1)–Cl(1) 91.85(7).

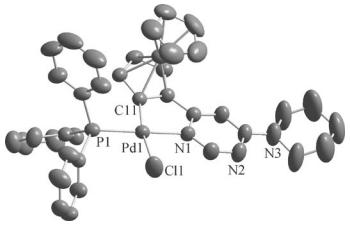



Figure 11. Molecular structure of **27**. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(11) 1.987(8), Pd(1)–N(1) 2.114(3), Pd(1)–P(1) 2.2345(9), Pd(1)–Cl(1) 2.3685(2) and C(11)–Pd(1)–N(1) 80.78(12), C(11)–Pd(1)–P(1) 93.18(10), P(1)–Pd(1)–Cl(1) 94.80(4), N(1)–Pd(1)–Cl(1) 91.95(7).

The molecular structure of **32** is shown in Figure 13. In **32**, DCPAB replaces $PPh_3$ in **15**. The Pd–P [2.2679(15) Å] bond length in **32** is longer than those in the other seven complexes [2.2322(11)–2.2454(18) Å] possibly due to the steric bulk of DCPAB. Unlike **15**, C–H···Cl hydrogen bonds are not found in **32**.

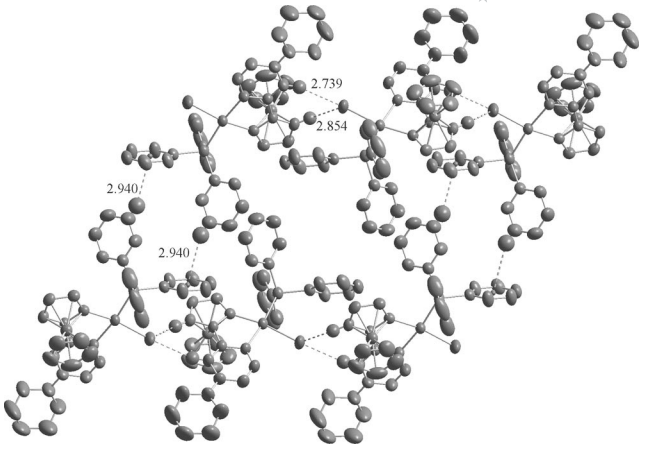



Figure 12. 2D lamellar structure of **27** showing the C–H···Cl(π) interactions. Thermal ellipsoids are drawn at 50% probability. Non-hydrogen bonding H atoms are omitted for clarity.

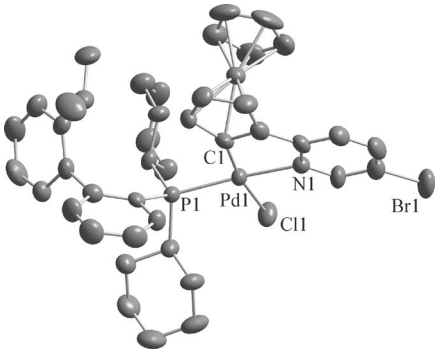



Figure 13. Molecular structure of **32**. Thermal ellipsoids are drawn at 50% probability. H atoms and $CH_2Cl_2$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 1.973(6), Pd(1)–N(1) 2.156(5), Pd(1)–P(1) 2.2679(15), Pd(1)–Cl(1) 2.3986(15) and C(1)–Pd(1)–N(1) 79.9(2), C(1)–Pd(1)–P(1) 95.25(17), P(1)–Pd(1)–Cl(1) 93.28(6), N(1)–Pd(1)–Cl(1) 92.21(13).

## Conclusions

We have developed an efficient method for the synthesis of palladacycles with polydentate ligands by a stepwise coupling route without additional palladium catalysis. A small percentage of the halide-containing palladacycle acted as a precatalyst and the remainder behaved as the substrate in the coupling reaction. The advantages of this method include good substrate generality, high efficiency, and that additional catalysis is not required. A series of new ferrocenyl palladacycles with polydentate ligands were successfully synthesized by Suzuki and C–N coupling reactions. Single-crystal X-ray analysis confirms that there are many types of intermolecular C–H···Cl (O, N, π) interactions and π–π interactions in the structures of these palladacycles. Subsequent work will focus on the synthesis of polynuclear or heteropolymetallic palladacycles by this method.

## Experimental Section

**Materials and Instrumentation:** All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were commercially available except for chloromercuriferrocene,[25] **b**,[9] **1**,[9] and **31**,[4e] which were prepared according to the published procedures. Melting points were measured using a WC-1 microscopic apparatus. Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. IR spectra were collected with a Bruker VECTOR22 spectrophotometer as KBr pellets. $^1$H NMR spectra were recorded with a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were measured with a LC-MSD-Trap-XCT instrument.

**[(η$^5$-$C_5H_5$)]Fe[(η$^5$-$C_5H_3$)$NC_5H_3$Br] (14):** In a flask equipped with a reflux condenser and gas inlet, chloromercuriferrocene (1 mmol), 2,5-dibromopyridine (1.1 mmol), NaI (2 mmol), $Pd(PPh_3)_4$ (0.05 mmol), dry tetrahydrofuran (18 mL), and dry $Me_2CO$ (12 mL) were placed under a $N_2$ atmosphere. The reaction mixture was heated at 80 °C for 5 h, cooled, and quenched with water. The organic layer was separated, and the aqueous layer was extracted with dichloromethane, the combined organic layers were washed with water, dried with $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The product was purified by passing it through a short column of silica gel with $CH_2Cl_2$/petroleum ether (2:1) as eluent. The second band was collected and afforded **14** as a red solid; yield 65%; m.p.: 111–112 °C. $C_{15}H_{12}BrFeN$ (342.02): calcd. C 52.68, H 3.54, N 4.10; found C 52.87, H 3.32, N 4.31. IR (KBr): $\tilde{\nu}$ = 3075, 3021, 1569, 1489, 1437, 1388, 1367, 1283, 1375, 1200, 1101, 1026, 1001, 889, 840, 825, 752, 695 cm$^{-1}$. ESI$^+$-MS: *m*/*z* = 342.0 [M + H]$^+$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.53 (s, 1 H, Ar–H), 7.67 (d, 1 H, Ar–H), 7.28 (d, 1 H, Ar–H), 4.88 (s, 1 H, $C_5H_3$), 4.41 (s, 1 H, $C_5H_3$), 4.05 (s, 5 H, $C_5H_5$) ppm.

**General Procedure for the Synthesis of 15 and 32:** A mixture of **14** (1 mmol), $Li_2PdCl_4$ (1.1 mmol), and NaOAc (1 mmol) in dry methanol (20 mL) was stirred for 24 h at room temperature. The red solids (yield: 85%) were collected by filtration and washed several times with methanol, and can be assigned as a dimeric complex of palladium.[1] Because of its poor solubility in common solvents, it was treated, without further purification, with the monophosphane ligand ($PPh_3$ or DCPBA) (1.1 mmol) in dry $CH_2Cl_2$ at room temp. for 1 h. The product was purified by passing it through a short column of silica gel with $CH_2Cl_2$ as eluent. The first band was collected and afforded **15** or **32**.

**[PdCl({(η$^5$-$C_5H_5$)}Fe{(η$^5$-$C_5H_3$)$NC_5H_3$Br})($PPh_3$)] (15):** Red solid; yield 93%; m.p.: 219–220 °C. $C_{33}H_{26}BrClFeNPPd$ (745.15): calcd. C 53.19, H 3.52, N 1.88; found C 53.32, H 3.26, N 1.99. IR (KBr): $\tilde{\nu}$ = 3120, 1592, 1494, 1433, 1391, 1308, 1238, 1188, 1159, 1099, 1026, 993, 906, 852, 816, 746, 695 cm$^{-1}$. ESI$^+$-MS: *m*/*z* = 708.9 [M – Cl]$^+$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.46 (s, 1 H, Ar–H), 7.78–7.86 (m, 6 H, Ar–H), 7.76 (d, 1 H, Ar–H), 7.27–7.47 (m, 9 H, Ar–H), 7.16 (d, 1 H, Ar–H), 4.59 (s, 1 H, $C_5H_3$), 4.11 (s, 1 H, $C_5H_3$), 3.71 (s, 5 H, $C_5H_5$), 3.33 (s, 1 H, $C_5H_3$) ppm.

**[PdCl({(η$^5$-$C_5H_5$)}Fe{(η$^5$-$C_5H_3$)$NC_5H_3$Br})(DCPAB)] (32):** Red solid; yield 85%; m.p.: 192–193 °C. $C_{41}H_{47}BrClFeN_2PPd$ (876.41): calcd. C 56.19, H 5.41, N 3.20; found C 56.33, H 5.22, N 3.38. IR (KBr): $\tilde{\nu}$ = 3046, 2924, 2849, 1589, 1492, 1444, 1375, 1304, 1259, 1188, 1109, 1042, 1022, 993, 943, 847, 814, 734 cm$^{-1}$. ESI$^+$-MS: *m*/*z* = 840.1 [M – Cl]$^+$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.42 (s, 1 H, Ar–H), 7.73 (s, 1 H, Ar–H), 7.12–7.32 (m, 9 H, Ar–H), 4.53 (s, 1 H, $C_5H_3$), 4.29 (s, 1 H, $C_5H_3$), 3.90 (s, 5 H, $C_5H_5$), 3.19 (s, 1 H, $C_5H_3$), 2.53 (s, 6 H, $NMe_2$), 3.33 (s, 1 H, $C_5H_3$), 1.26–2.09 (m, 22 H, $PCy_2$) ppm.

**General Procedure for Palladacycles with Polydentate Ligands by Stepwise Suzuki Coupling Reactions:** In a Schlenk tube, a mixture of halide-containing palladacycle (0.5 mmol), arylboronic acid (0.5–2.5 mmol), and base (1.0 mmol) in solution (5 mL) was evacuated and charged with nitrogen. The reaction mixture was heated at 110 °C for 16–24 h, cooled, and quenched with water. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, dried with $MgSO_4$, filtered, the solvent was removed on a rotary evaporator, and the products were isolated by flash chromatography on silica gel. Data for a selected example:

**[PdCl({(η$^5$-$C_5H_5$)}Fe{(η$^5$-$C_5H_3$)$NC_5H_3NC_5H_3N(CH_3)_2$})($PPh_3$)] (21):** Red solid; yield 90%; m.p.: 239–240 °C. $C_{40}H_{35}ClFeN_3PPd$ (786.41): calcd. C 61.09, H 4.49, N 5.34; found C 61.31, H 4.25, N 5.55. IR (KBr): $\tilde{\nu}$ = 3048, 2935, 1604, 1545, 1498, 1435, 1404, 1380, 1221, 1180, 1155, 1098, 1001, 952, 812, 749, 697 cm$^{-1}$. ESI$^+$-MS: *m*/*z* = 751.1 [M – Cl]$^+$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.82 (s, 1 H, Ar–H), 8.46 (s, 2 H, Ar–H), 7.83 (m, 8 H, Ar–H), 7.41 (m, 9 H, Ar–H), 7.28 (d, 1 H, Ar–H), 6.58 (d, 1 H, Ar–H), 4.61 (s, 1 H, $C_5H_3$), 4.06 (s, 1 H, $C_5H_3$), 3.68 (s, 5 H, $C_5H_5$), 3.37 (s, 1 H, $C_5H_3$), 3.12 (s, 6 H, $CH_3$) ppm. For other new compounds, see Supporting Information.

**General Procedure for Palladacycles with Polydentate Ligands by C–N Coupling Reactions:** In a Schlenk tube, a mixture of halide-containing palladacycle (0.5 mmol), amine (0.75 mmol) or base (1.0 mmol) in solution (5 mL) was evacuated and charged with nitrogen. The reaction mixture was heated at 110 °C for 24 h. The work up was the same as described above for the Suzuki reaction. Data for a selected example:

**[PdCl({(η$^5$-$C_5H_5$)}Fe{(η$^5$-$C_5H_3$)$N_2C_4H_2NHC_6H_4CH_3$})($PPh_3$)] (23):** Red solid; yield 89%; m.p.: 246–247 °C. $C_{39}H_{33}ClFeN_3PPd$ (772.38): calcd. C 60.65, H 4.31, N 5.44; found C 60.91, H 4.12, N 5.64. IR (KBr): $\tilde{\nu}$ = 3079, 2924, 1602, 1507, 1436, 1398, 1302, 1258, 1184, 1151, 1097, 1022, 997, 813, 748, 695 cm$^{-1}$. ESI$^+$-MS: *m*/*z* = 736.1 [M–Cl]$^+$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.32 (s, 1 H, Ar–H), 7.81 (m, 6 H, Ar–H), 7.43 (m, 9 H, Ar–H), 7.33 (d, 2 H, Ar–H), 7.25 (d, 2 H, Ar–H), 6.50 (s, 1 H, Ar–H), 4.54 (s, 1 H, $C_5H_3$), 4.13 (s, 1 H, $C_5H_3$), 3.71 (s, 5 H, $C_5H_5$), 3.34 (s, 1 H, $C_5H_3$), 2.39 (s, 1 H,$CH_3$) ppm. For other new compounds, please see Supporting Information.

**X-ray Crystal Structure Determination**: Crystallographic data were collected with a Bruker SMART APEX-II CCD diffractometer with Mo-$K_\alpha$ radiation ($\lambda$ = 0.071073 Å) at room temperature. The data were corrected for Lorentz-polarization factors and absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on $F^2$ with the SHELX-97 program.[26] An empirical absorption correction was applied using the SADABS program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in geometrically calculated positions. The details of crystal structure determination of the eight complexes discussed are summarized in Table 7.

CCDC-804625 (for **3**), -800308 (for **10**), -808329 (for **11**), -804624 (for **15**), -804623 (for **17**), -824513 (for **26**), -800310 (for **27**), and -804897 (for **32**) 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.

**Supporting Information** (see footnote on the first page of this article): General comments, synthesis and characterization data (melt-

Table 7. Crystallographic data and structure refinement for **3**·$2CH_2Cl_2$, **10**, **11**, **15**, **17**·$(CH_2Cl_2)_{0.5}$, **26**, **27**, and **32**·$2CH_2Cl_2$.

| | **3**·$2CH_2Cl_2$ | **10** | **11** | **15** |
|---|---|---|---|---|
| Formula | $C_{44}H_{36}Cl_5FeN_2PPd$ | $C_{39}H_{31}ClFeN_3O_2PPd$ | $C_{80}H_6Cl_2Fe_2N_6O_4P_2Pd_2$ | $C_{33}H_{26}BrClFeNPPd$ |
| $M_r$ | 963.22 | 802.34 | 1632.73 | 745.13 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ |
| $a$ [Å] | 10.7161(18) | 22.989(5) | 11.5196(9) | 9.3489(9) |
| $b$ [Å] | 14.179(2) | 9.3512(19) | 17.9889(13) | 16.0727(15) |
| $c$ [Å] | 15.680(3) | 17.663(4) | 38.505(3) | 19.7101(18) |
| $\alpha$ [°] | 69.002(2) | 90 | 90 | 90 |
| $\beta$ [°] | 70.677(2) | 105.97(3) | 96.2740(10) | 91.1970(10) |
| $\gamma$ [°] | 69.303(2) | 90 | 90 | 90 |
| $V$ [Å$^3$] | 2022.9(6) | 3650.6(13) | 7931.4(10) | 2961.0(5) |
| $D_c$ [g cm$^{-3}$] | 1.581 | 1.460 | 1.367 | 1.671 |
| $Z$ | 2 | 4 | 4 | 4 |
| $F$(000) | 972 | 1624 | 3312 | 1480 |
| GOF | 1.036 | 1.071 | 1.026 | 1.001 |
| $R_1$, w$R_2$ | 0.0520, | 0.0773, | 0.0459, | 0.0363, |
| $[I > 2\sigma(I)]$[a] | 0.1478 | 0.2408 | 0.0909 | 0.0764 |
| $R_1$, w$R_2$ | 0.0654, | 0.0958, | 0.0910, | 0.0655, |
| (all data) | 0.1602 | 0.2604 | 0.1010 | 0.0897 |
| | **17**·$(CH_2Cl_2)_{0.5}$ | **26** | **27** | **32**·$2CH_2Cl_2$ |
| Formula | $C_{77}H_{62}Cl_4Fe_2N_4P_2Pd_2$ | $C_{39}H_{39}Cl_3FeN_3PPd$ | $C_{37}H_{35}ClFeN_3PPd$ | $C_{43}H_{51}BrCl_5FeN_2PPd$ |
| $M_r$ | 1571.55 | 849.30 | 750.35 | 1046.24 |
| Crystal system | orthorhombic | triclinic | monoclinic | monoclinic |
| Space group | $P2(1)2(1)2(1)$ | $P\bar{1}$ | $P2_1/c$ | $P2(1)$ |
| $a$ [Å] | 9.970(2) | 10.0708(9) | 23.912(2) | 10.1963(9) |
| $b$ [Å] | 19.760(4) | 13.3732(12) | 9.2147(9) | 19.2579(16) |
| $c$ [Å] | 33.830(7) | 16.1276(14) | 17.5050(17) | 11.4529(10) |
| $\alpha$ [°] | 90 | 89.3420(10) | 90 | 90 |
| $\beta$ [°] | 90 | 79.3680(10) | 96.3810(10) | 98.7990(10) |
| $\gamma$ [°] | 90 | 72.5340(10) | 90 | 90 |
| $V$ [Å$^3$] | 6665(2) | 2034.1(3) | 3833.1(6) | 2222.4(3) |
| $D_c$ [g cm$^{-3}$] | 1.566 | 1.300 | 1.300 | 1.563 |
| $Z$ | 4 | 2 | 4 | 2 |
| $F$(000) | 3176 | 864 | 1528 | 1060 |
| GOF | 1.051 | 1.060 | 1.016 | 1.022 |
| $R_1$, w$R_2$ | 0.0491, | 0.0345, | 0.0377, | 0.0440, |
| $[I > 2\sigma(I)]$[a] | 0.1390 | 0.0982 | 0.0914 | 0.1085 |
| $R_1$, w$R_2$ | 0.0568, | 0.0422, | 0.0568, | 0.0552, |
| (all data) | 0.1457 | 0.1029 | 0.0987 | 0.1166 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]\}^{1/2}$.

ing point, elemental analysis, IR, $^1$H NMR, and ESI-MS.) for all new compounds **2**–**13**, **16**–**20**, **22**, **24**–**30**, and **33**–**39**, and additional figures for structure of complexes **3**, **4**, **10**, **11**, **15**.

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