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Suzuki Coupling Reactions Catalyzed with Palladacycles and Palladium(II) Complexes of 2-Thiophenemethylamine-Based Schiff Bases: Examples of Divergent Pathways for the Same Ligand

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Activation of Suzuki coupling with a complex of palladium varies with the mode of coordination of its ligand. The moisture-/air-insensitive palladacycles and palladium complexes designed using the same ligand (Schiff base, coordinating as an N,C$^-$ and N,O$^-$ ligand, respectively) have been found to follow different pathways. Palladacycles are more efficient, as their 0.001 mol-% loading gives good conversion (yield > 90 %) in several cases. Higher loading than this is required for Pd complexes to obtain a similar yield. Activation with palladacycles involves the role of nanosized Pd-containing species generated in situ during catalysis, in which, as with Pd^{II} complexes, no such particle is formed and Pd^0 probably remains protected by the sulfur of the thienyl group. The Schiff bases used here were designed by the reaction of 2-thiophenemethylamine with 2-hydroxybenzophenone/2-hydroxy-4-methoxybenzophenone/2-hydroxyacetophenone (**L1/L2/L3**). Upon treatment with [$PdCl_2(CH_3CN)_2$] and [Na_2PdCl_4] they gave palladacycles [Pd**L1/L2**(CH_3CN)Cl] (**1/3**) and palladium(II) complexes [Pd(**L1/L2/L3**)$_2$] (**2/4/5**), respectively. Compounds **L1**–**L3** and their complexes **1**–**5** were authenticated with ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and HRMS. Single crystal structures of **1**, **2**, **4**, and **5** reveal nearly square-planar geometry around Pd in each case. The PPh_3/Hg poisoning and two-phase tests indicate that the catalysis is homogeneous for both the palladacycle and palladium complexes, probably through leaching of Pd^0 from NPs in the case of the former.

Introduction

Palladium species constitute a class of versatile and useful catalysts for C–C bond-forming reactions.[1,2] The facile interchange between oxidation states and the tolerance of palladium compounds toward many functional groups (owing to mild reaction conditions) are mainly responsible for their versatility.[2] Of the various C–C bond-forming reactions, Suzuki–Miyaura coupling (SMC) is very important[3] as the biaryl derivatives prepared by this coupling have promising roles in the production of pharmaceutical ingredients, agrochemicals, and natural products[4] for industrial purposes. Complexes of Pd^{II} with bulky and electron-rich phosphines,[5,6] carbenes,[7] palladacycles,[8,9] and organochalcogens,[10] as well as palladium chacogenide/phosphide nanoparticles[10b] are among the high-efficiency moieties for Suzuki–Miyaura coupling. Many of these species are also attractive owing to the ease with which they can be modified. In a very large number of cases, such coupling reactions are performed under an inert atmosphere because many of the known good catalytic species are sensitive to oxygen or moisture.[11] Therefore Suzuki coupling reactions that give high yield under aerobic conditions continue to be an important challenge. Another challenge is to rationalize variation in catalytic efficiency of various palladium moieties. Palladium(II) complexes of Schiff bases[12] have emerged as a family of phosphine-free, air- and moisture-insensitive efficient catalysts. Palladacycles and Pd complexes of pincer ligands in the family of Suzuki catalysts are generally considered to be species that show high performance. However, a straight comparison of palladacycles with Pd^{II} complexes, when both are formed with the same ligand, is not known. Such comparison can easily be envisaged as being important to offer an in-depth understanding of the higher efficiency of palladacycles relative to Pd complexes and in turn in identifying a rationalization for the difference in their performances. Herein we report that activation of SMC with a palladium(II) complex varies with the mode of coordination of its ligand. Palladacycles and palladium complexes designed using a Schiff base (coordinating as an N,C$^-$ and N,O$^-$ ligand, respectively) have been found to follow different pathways. In view of this, this pa-

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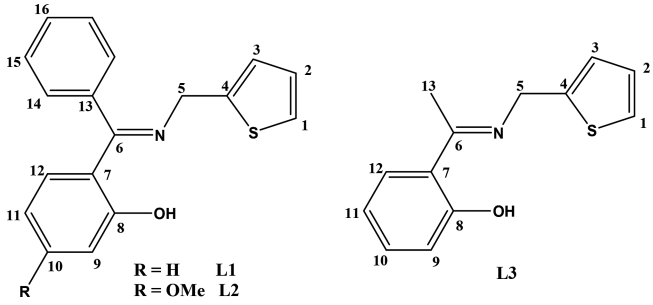
per focuses on the design of Schiff base ligands that contain a thiophene ring (**L1–L3**), as their synthesis and use in preparing a catalyst for Suzuki–Miyaura coupling reaction is not known, and it is shown that thienyl can protect the catalytically active species if required. Palladacycles and Pd^{II} complexes (**1–5**) of these ligands have been prepared and explored for Suzuki–Miyaura coupling reactions. The in situ formation of Pd-containing NPs has been reported in Suzuki–Miyaura coupling reactions catalyzed with palladacycles[9b] of the organosulfur ligand as well as Pd complexes of sulfated Schiff bases.[12c]

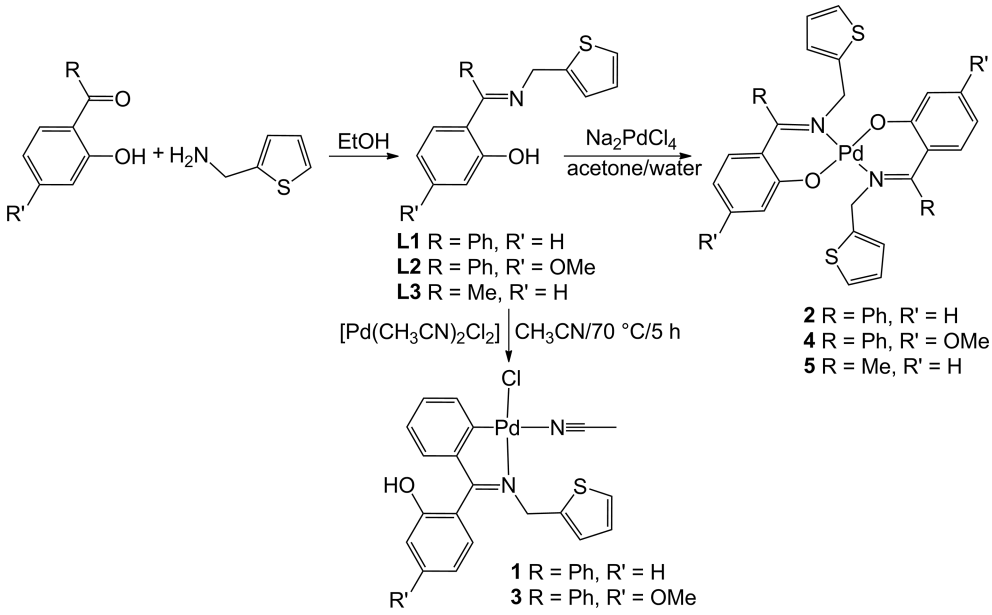


These NPs are stabilized with additives,[9g] and in their absence by ligands or their fragments.[7d] There is enough evidence to suggest that Pd^0 species leached from the surface of such NPs are the true catalysts for SMC. The size, dispersion, and the chemical nature of these NPs can be affected by the bonding mode of the ligand. Thus NPs might be considered for a rationalization of their catalytic performances. In the case of Pd^{II} complexes, the formation of Pd-based NPs was not noticed, whereas in the case of palladacycles it occurs instantaneously at the start of the coupling reaction. The in situ formation of NPs appears to be a possible reason for the higher performance of palladacycles relative to Pd complexes. It is probable that aggregation of Pd^0 to give NPs is prevented by additional protection with thienyl sulfur in the case of Pd complexes. All these results are part of this paper.

Results and Discussion

The preparations of ligands (**L1**, **L2**, and **L3**) and their palladium(II) complexes (**1**–**5**) are summarized in Scheme 1. The syntheses of complexes **1**–**4** require a palladium precursor and are solvent-dependent. Reaction of **L1** and **L2** with $[Pd(CH_3CN)_2Cl_2]$ in acetonitrile at 70 °C resulted in palladacycles **1** and **3**, respectively, whereas treating **L1**–**L3** with Na_2PdCl_4 in an acetone/water (1:1) mixture at room temperature isolated Pd^{II} complexes **2**, **4**, and **5**. In an acetone/water mixture the reactions of $[Pd(CH_3CN)_2Cl_2]$ with ligands did not result in palladacycles, even at 70 °C. Similarly, Na_2PdCl_4 did not give a palladacycle upon reaction with the ligands in CH_3CN, even at 70 °C. It is probable that the $[Pd\{L = (N,O^-)_2\}]$ complex is first formed in the reaction of both Pd precursors and it remains stable in an acetone/water mixture, therefore it cannot be isolated. In coordinating CH_3CN it becomes labile, thereby finally resulting in a palladacycle. The yellow solids **1**, **2**, **4**, and **5** were found to be stable enough to store under ambient conditions for three months (as evidenced by their proton NMR spectra). The solubility of **L1**–**L3** in common organic solvents – namely, DMF, DMSO, CH_3CN, CH_2Cl_2, $CHCl_3$, and THF – was found to be good. Complexes **1** to **5** show good solubility in DMF, DMSO, CH_3CN, CH_2Cl_2, and $CHCl_3$. They are sparingly soluble in CH_3OH, diethyl ether, and THF, and negligibly soluble in hexane.

The air-insensitive ligands **L1**–**L3** and their Pd complexes **1**–**5** were characterized with ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **L1**–**L3** and complexes **1**–**5** (see Figures S19–S33 in the Supporting Information) were found to be consistent with



Scheme 1. Synthesis of ligands and their Pd^{II} complexes.

their molecular structures (Scheme 1). In the ^{1}H NMR spectra of **L1**, **L2**, and **L3**, the signals of the OH proton were observed at δ = 15.15, 15.88, and 15.64 ppm, respectively.[13] Upon formation of palladacycles **1** and **3**, the signal of the OH proton in the ^{1}H NMR spectra is shielded and appears at a position of approximately δ = 12.0–13.0 ppm. In the ^{1}H NMR spectra of complexes **2**, **4**, and **5**, the signal of the OH proton was found to be absent as the deprotonated OH group is coordinated to Pd. The ^{13}C{^{1}H} NMR spectrum of complex **1** has a new quaternary carbon signal at δ = 163.3 ppm, which shows the palladation of **L1**, whereas in the case of **2**, **4**, and **5**, no such signal was observed. In the mass spectra of Schiff base ligands **L1**, **L2**, and **L3**, the peaks that appear at 294.0947, 324.1053, and 232.0791, respectively, have been ascribed to the $[M + H]^+$ ion (see Figures S3–S8). The mass spectra of complexes **1** and **3** show peaks at 690.0633 and 751.0924, which might be ascribed to the $[(L)_2Pd]^+$ fragment of the corresponding complex (see Figures S9, S10, S13, and S14). This surprising species is most likely formed as the loss of two CH_3CN ligands is followed by the capture of **L**. The mass spectra of complexes **2** and **5** show peaks at 713.0531 and 589.0215, which have been ascribed to the $[M + Na]^+$ fragment (Na comes from sodium formate; see the Experimental Section) of the corresponding complex (see Figures S11, S12, S17, and S18), whereas in the mass spectrum of complex **4** $[M + H]^+$, the fragment peak was noticed at 751.0924 (see Figures S15 and S16).

Crystal Structure

The crystal and refinement data of complexes **1**, **2**, **4**, and **5** are given in Table S1 of the Supporting Information, and their molecular structures (ellipsoids at 30% probability level) are shown in Figures 1, 2, 3, and 4 with selected bond lengths and angles (more values are given in Tables S2–S5). Our attempts to crystallize complex **3** were unsuccessful.

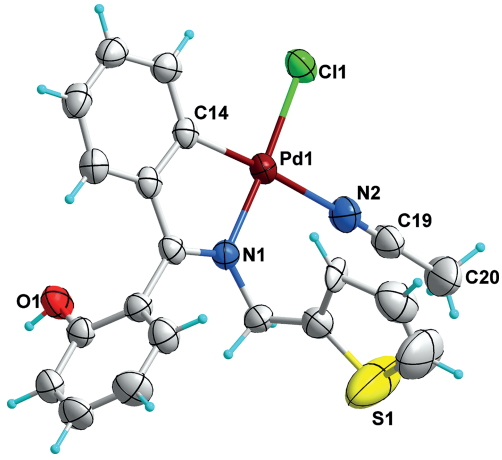


Figure 1. Molecular structure of **1**. Bond lengths [Å]: C14–Pd1 1.979(4), N1–Pd1 2.034(4), Cl1–Pd1 2.3257(13), N2–Pd1 2.127(5). Bond angles [°]: C6–N1–Pd1 116.0(3), C19–N2–Pd1 175.7(5), C14–Pd1–N1 80.89(16), C14–Pd1–N2 175.12(17), N1–Pd1–N2 94.28(16).

Palladium adopts a nearly square-planar geometry in all of the complexes. Ligands **L1** and **L2** are coordinated with Pd in a bidentate N,C$^-$ mode, thus forming a five-membered chelate ring in the case of palladacycle **1**. Ligands **L1** to **L3** are coordinated with Pd in a bidentate N,O$^-$ mode in the case of **2**, **4**, and **5**. Each of the two ligands forms a six-membered chelate ring with Pd. The Pd–N1 bond lengths in **1**, **2**, **4**, and **5** [2.023(4)–2.044(3) Å] are consistent with the reported values [2.002(2)–2.010(4) Å] for Pd^{II} complexes of tridentate selenated Schiff bases[14] but somewhat longer than the value of 1.986(6) Å reported[14] for $[PdCl\{(C_6H_5)(C_6H_4\text{–}2\text{-}O\text{–})C{=}N(CH_2)_3SePh\}]$. The Pd–C

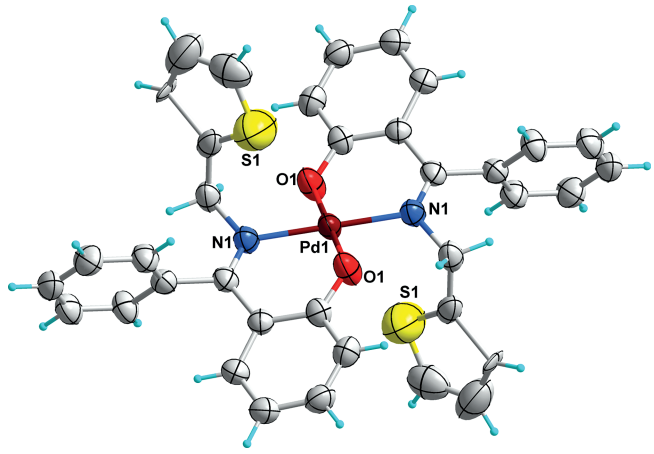


Figure 2. Molecular structure of **2**. Bond lengths [Å]: N1–Pd1 2.023(4), O1–Pd1 1.972(4). Bond angles [°]: C6–N1–Pd1 125.2(4), C5–N1–Pd1 114.9(3), C8–O1–Pd1 123.1(3), O1–Pd1–O1 180.0(2), O1–Pd1–N1 90.52(18).

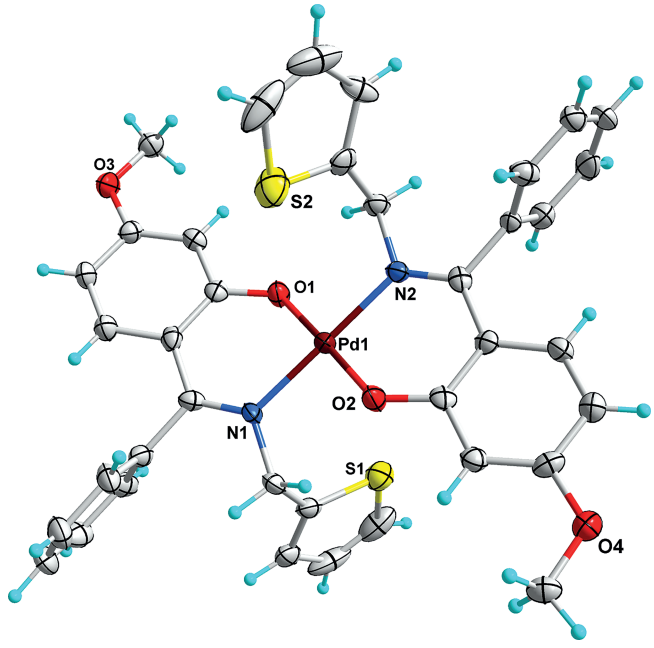


Figure 3. Molecular structure of **4**. Bond lengths [Å]: N1–Pd1 2.028(3), N2–Pd1 2.022(3), O1–Pd1 1.980(3), O2–Pd1 1.979(3). Bond angles [°]: O2–Pd1–O1 178.40(13), O2–Pd1–N2 90.20(12), C5–N1–Pd1 114.7(2), C25–N2–Pd1 125.8(3).

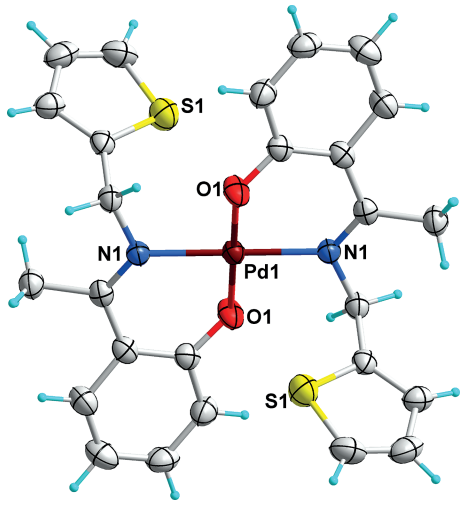


Figure 4. Molecular structure of **4**. Bond lengths [Å]: N1–Pd1 2.044(3), O1–Pd1 1.974(2). Bond angles [°]: C5–N1–Pd1 114.4(2), C8–O1–Pd1 123.9(2), O1–Pd1–O1 180.0, O1–Pd1–N1 89.43(11).

distance [1.979(4) Å] of **1** is consistent with the value of 1.971(16) Å[9d] reported earlier for this kind of a palladium(II)–(S,C,S) pincer complex bond. The Pd–Cl bond length of **1** [2.326(13) Å] is also consistent with the value [2.3159(7) Å] reported for the Pd^{II} complex of a tridentate sulfated Schiff base.[14] The Pd–O1 bond lengths of **2**, **4**, and **5** [1.972(4)–1.980(3) Å] are consistent with the values of 1.993(3)–1.986(16) Å reported for Pd^{II} complexes of tridentate sulfated Schiff bases.[14] In the crystals of **1**, **2**, **4**, and **5** there are secondary interactions (see Figures 5, 6, as well as Figures S1–S2). Tables S6 and S7 show interatomic distances. The head-to-tail arrangement of chelating N,O ligands observed in the case of complexes **2**, **4**, and **5** is worth mentioning.

The intermolecular O1–H23···Cl1 [2.342 Å] interactions in **1**, C14–H14···π [2.664 Å] interactions in **2**, and C2–H2···O1 [2.611 Å] interactions in **5** result in chain structures.

Applications in Suzuki–Miyaura Coupling Reactions

The stability of organoboronic acids and the formation of nontoxic byproducts have increased the appeal of Suzuki–Miyaura coupling protocols with several industrial applications.[15] The activation of this reaction is not restricted to a homogeneous protocol, but in recent years heterogeneous catalytic systems[16,17] have been developed for it. Complexes **1** to **5** were investigated for the Suzuki–Miyaura coupling reaction. The results given in Tables 1 and 2 suggest that complexes **1**–**5** are efficient for this coupling, as good yields were obtained even with deactivated substrates such as 4-bromoanisole with low palladium loading. For the reaction between 4-bromobenzaldehyde and phenylboronic acid under aerobic conditions at 90 °C for 10 h (catalyzed with **1**), different bases and solvents were explored (see Table S8 in the Supporting Information). The yield of coupled product was found to be approximately 81% when EtOH was used as the reaction medium and K_2CO_3 was used as base. However, the best results were obtained at 90 °C (bath temperature) with K_2CO_3 and DMF (3 mL)/H_2O (2 mL). At room temperature, the yield of biaryl was found to be 43% with 0.5 mol-% loading of catalyst **1** (Table S8). The catalytic efficiency of palladacycles **1** and **3** is higher than those of Pd^{II} complexes **2**, **4**, and **5**. The ligands in all complexes are the same or similar. Thus the present results give a direct comparison of palladacycles with palladium(II) complexes, with minimized ligand factors, which indicates the superiority of the former on the

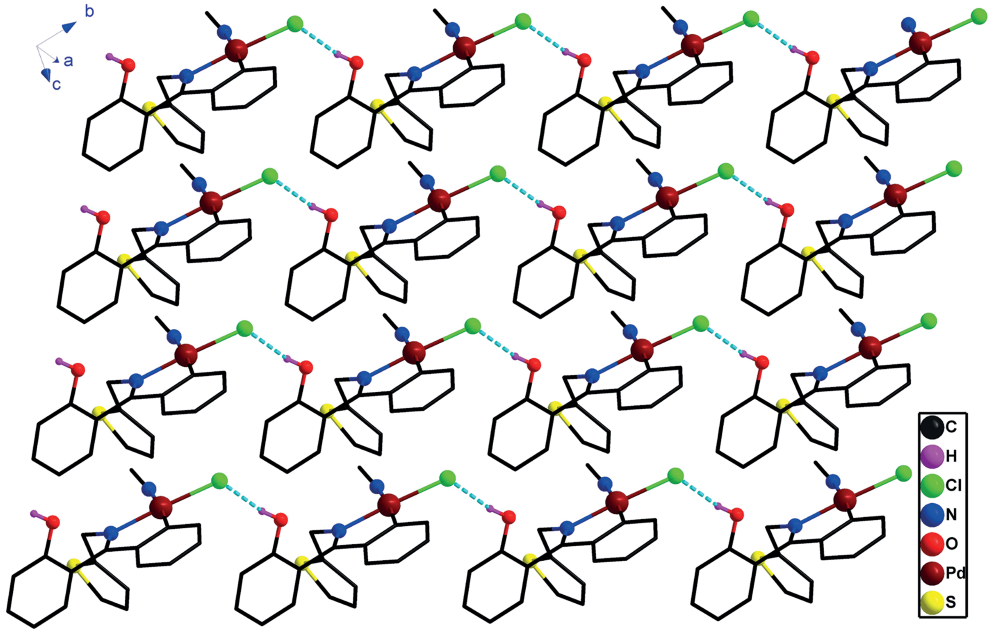


Figure 5. Intermolecular interactions in complex **1**.

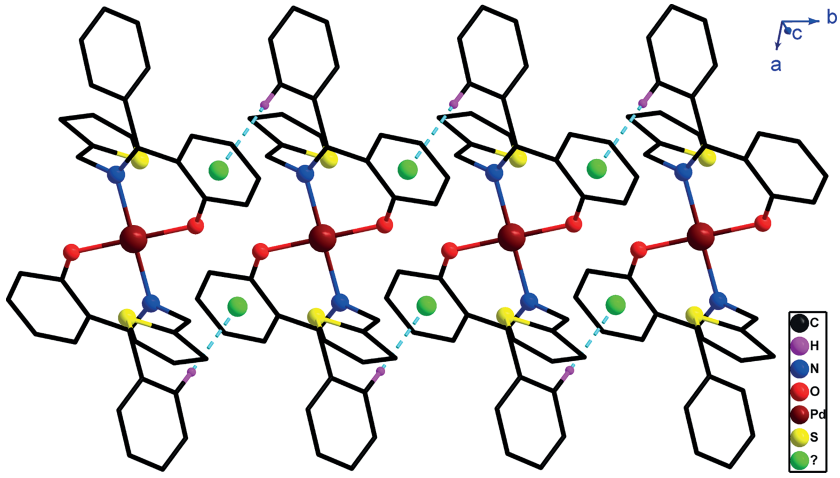
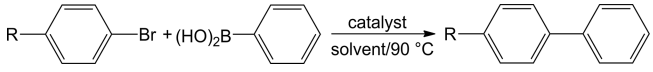


Figure 6. Intermolecular interactions in complex **2**.

basis of experimental results with palladacycle or palladium(II) complexes alone, irrespective of the difference in ligands. Among palladacycles **1** and **3** the activity of **3** (in which OMe group is present) is a bit higher.

Table 1. Suzuki–Miyaura coupling reaction catalyzed by using **1** and **3**.[a]



Entry	Aryl halide	Pd [mol-%]	Yield[b] [%]	
			1	**3**
1	4-bromobenzaldehyde	0.001	92	95
2	4-bromobenzonitrile	0.001	90	94
3	1-bromo-4-nitrobenzene	0.001	87	91
4	4-bromoacetophenone	0.001	89	93
5	2-bromobenzaldehyde	0.01	88	91
6	2-bromoacetophenone	0.01	87	92
7	4-bromobenzoic acid	0.1	90	94
8	bromobenzene	0.01	89	92
9	4-bromotoluene	0.001	84	93
10	4-bromoanisole	0.001	82	91
11	2-bromopyridine	0.001	91	94
12	3-bromopyridine	0.001	87	93
13	4-bromopyridine	0.001	90	95
14	3-bromoquinoline	0.01	86	91

[a] Reaction conditions: 1.0 equiv. of aryl halide, 1.5 equiv. of phenylboronic acid, 2 equiv. of K_2CO_3, DMF (3 mL)/H_2O (2 mL) as solvent, reaction time 10 h, and temperature of bath 90 °C. [b] Isolated yield.

The scope of the present activation of Suzuki–Miyaura coupling can be understood from Tables 1 and 2. When the reaction between 4-bromobenzaldehyde and phenylboronic acid was carried out with 0.001 mol-% of complex **4**, the yield of the coupled product was found to be 63%. Thus N,O⁻ chelates are roughly 30% slower. In the course of Suzuki reactions catalyzed with **1** and **3**, the solution turned black immediately upon mixing the reactants, whereas in the case of **2**, **4**, and **5** no such blackening was observed. Thus in the case of activation with **2**, **4**, and **5**, homogeneous catalysis is most likely. The Pd^0 required for initiating Suzuki coupling is probably stabilized as a complex by the

Table 2. Suzuki–Miyaura coupling reaction catalyzed by using **2**, **4**, and **5**.[a]

Entry	Aryl halide	Pd [mol-%]	Yield[b] [%]		
			2	**4**	**5**
1	4-bromobenzaldehyde	0.01	94	96	87
2	4-bromobenzonitrile	0.01	91	93	86
3	1-bromo-4-nitrobenzene	0.01	86	90	81
4	4-bromoacetophenone	0.01	91	95	86
5	2-bromobenzaldehyde	0.01	85	90	78
6	2-bromoacetophenone	0.01	84	91	79
7	4-bromobenzoic acid	0.1	82	88	81
8	bromobenzene	0.1	88	93	83
9	4-bromotoluene	0.01	81	86	74
10	4-bromoanisole	0.01	79	85	73
11	2-bromopyridine	0.01	90	94	78
12	3-bromopyridine	0.01	88	92	76
13	4-bromopyridine	0.01	90	95	78
14	3-bromoquinoline	0.1	85	90	71

[a] Reaction conditions: 1.0 equiv. of aryl halide, 1.5 equiv. of phenylboronic acid, 2 equiv. of K_2CO_3, DMF (3 mL)/H_2O (2 mL) as solvent, reaction time 10 h, and temperature of bath 90 °C. [b] Isolated yield.

thienyl-group sulfur after cleavage of the Pd–O bond. It is possible that **1** and **3** behave like a precatalyst and black particles formed at the beginning of the reaction are Pd-containing species, which have a role in the catalytic process. Easy formation of NPs in the case of palladacycles is corroborated by their thermogravimetric analysis (TGA; see Figures S36 and S37 in the Supporting Information), which shows their decomposition before 90 °C, the temperature of the coupling reaction. However, chelates **2**, **4**, and **5** show signs of decomposition in TGA around 200 °C. In high-temperature Suzuki coupling, the combined effect of temperature, base, and solvent system results in Pd^0 formation.[18] In the present case, the S of the thienyl group is nearby, which probably weakly coordinates with Pd^0 to make it stable. The palladacycles decompose and therefore any stabilization from the thienyl group is ruled out. The variation observed in catalytic efficiency with the presence of an –OMe group might be due to some difference between

the black species generated in situ during the course of activation with **1** and **3**, respectively.

The black particles formed from **1** and **3** during the course of catalysis of the coupling reaction of 4-bromobenzaldehyde with $PhB(OH)_2$ under optimum reaction conditions were isolated (see the Experimental Section) and analyzed in detail to establish the possibility of a correlation between the catalytic activity and nature of the black particles (which were envisaged to be true catalysts or playing a role in the catalysis). The SEM-EDX (see Figures S34 and S35 in the Supporting Information) and HRTEM (Figure 7) images of these black particles suggest that they are nanosized and spherical in shape. They contain Pd and S. On the basis of EDX analysis, the Pd/S ratio is nearly 7:1 and 6:1 in terms of NPs with **1** and **3**, respectively. They are stable in solution as well as in the solid state. The size of 90–95% of these NPs is between approximately 2 and 4 nm (see Figure 8). The marginal difference in the efficiency of **1** and **3** might be ascribed to a larger population of small-sized NPs generated from **3** relative to **1** and some difference in their dispersion (more in case of **3**). In the case of **2** and **4**, the –OMe group makes a difference of 5–6% in the yield. This small difference need not be accounted for in view of order of error (ca. 2%) in determining the yield.

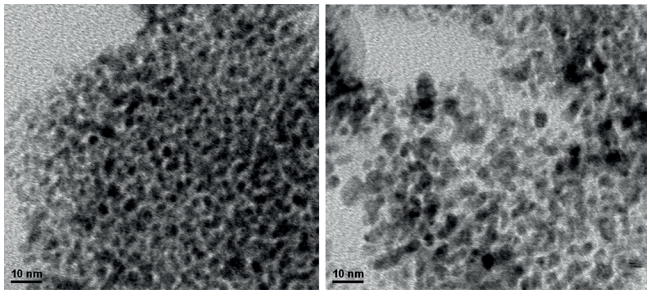


Figure 7. HRTEM micrographs of NPs (left) **1** and (right) **3** isolated from complexes **1** and **3** during Suzuki–Miyaura coupling.

Mercury poisoning and PPh_3 tests were found to be negative. Therefore, to identify whether the reactions catalyzed with **1** and **3** were heterogeneous or homogeneous, a two-phase test[19] was carried out with complex **1**, as in the absence of clear-cut poisoning tests there is the possibility of involvement of surface Pd atoms of nanoparticles in oxidative addition to form a soluble Pd^{II} intermediate Ar–Pd–Br and driving the catalysis homogeneously thereafter also exists.[20] This test (called a three-phase test when the catalyst is a solid phase), developed by Rebek and coworkers,[19] is considered to be more definitive when determining the presence of metal species that are homogeneously catalytically active. The test involves covalent immobilization of one of the reaction partners. 4-Bromobenzoic acid was immobilized on silica in the present case.

If the catalyst behaves in a heterogeneous fashion, the immobilized substrate is not expected to be converted to a coupled product. When Pd is released (i.e., catalysis is homogeneous), the anchored substrate can be converted to product. The addition of a soluble aryl halide to the reaction mixture ensures the presence of a catalytic process and its real active species.

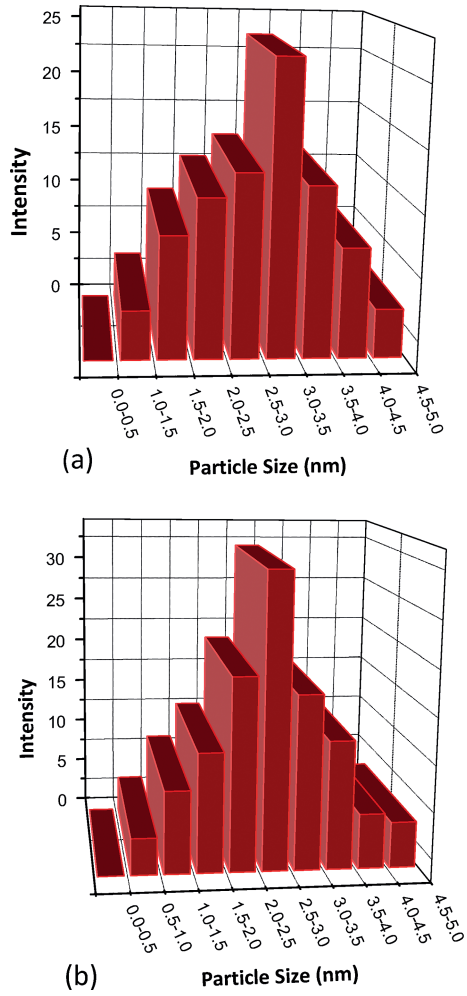
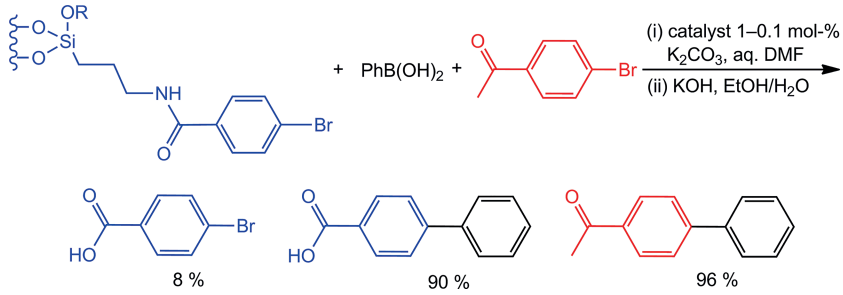


Figure 8. Size-distribution curve of NPs isolated from complexes (a) **1** and (b) **3**.

The two-phase test carried out with an immobilized aryl bromide and complex **1** is shown in Scheme 2. 4-Bromoacetophenone and immobilized 4-bromobenzoic acid (as amide) were treated with phenylboronic acid under optimum reaction conditions. The soluble part was separated by filtration and analyzed with ^1H NMR spectroscopy after workup. The yield of the cross-coupled product (4-acetylbiphenyl) was found to be approximately 96%. The solid phase was hydrolyzed, and the resulting products after workup were analyzed with ^1H NMR spectroscopy. Of the immobilized 4-bromobenzoic acid (as amide), approximately 90% was converted into the cross-coupled product (biphenyl-4-carboxylic acid). This observation suggests that the catalytically active Pd atoms leach out from the NPs generated in situ and are probably responsible for carrying out catalysis homogeneously. The leaching might happen first and is followed by the oxidative addition required for coupling. The surface Pd atoms of nanoparticles undergo oxidative addition to form soluble Pd^{II} intermediate Ar–Pd–Br, and the catalysis is driven thereafter (homogeneously).



Scheme 2. Two-phase test for Suzuki–Miyaura coupling.

The catalysis in the present case is thus a largely homogeneous process and is probably combined with oxidative addition to Pd^0 at the surface of NPs (followed by leaching into solution). This is shown independently by the catalytic activity of nanoparticles for Suzuki coupling (Table 3). The isolated NPs appear to be somewhat deactivated relative to those generated in situ, as their amount needed (1.0 mol-% of Pd) for comparable conversion is greater than those of complexes. Some Pd might also be leached into the reaction mixture before isolation. This could result in lowering of the reactivity, which might be further reduced owing to some aggregation in the course of isolation. The isolated NPs are not recyclable. Thus **1** and **3** are most probably dispensers of NPs, which probably further generate homogeneous real Pd^0 catalysts. The level of catalytic activity of **3** for the coupling of aryl bromides as substrates is generally good. Such an observation is important in the context of designing efficient catalysts for Suzuki coupling.

Table 3. Suzuki–Miyaura coupling reactions catalyzed by isolated NPs.[a]

Entry	Aryl halide	NP1[b]	NP3[b]
1	4-bromobenzaldehyde	84	91
2	4-bromotoluene	72	81

[a] Reaction conditions: 1.0 equiv. of aryl halide, 1.5 equiv. of phenylboronic acid, 1.0 mol-% of Pd NPs, 2 equiv. of K_2CO_3, DMF (3 mL)/H_2O (2 mL) as solvent, reaction time 10 h, and temperature of bath 90 °C. [b] Isolated yield.

Conclusion

Schiff base ligands (**L1** to **L3**) were synthesized by reaction of 2-hydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, and 2-hydroxyacetophenone with 2-thiophenemethylamine, respectively. Their complexes **1** and **3** are formed by treating **L1** and **L2** with $[PdCl_2(CH_3CN)_2]$ in CH_3CN at 70 °C, whereas complexes **2**, **4**, and **5** resulted after treating **L1**–**L3** with Na_2PdCl_4 in acetone/water (1:1) at room temperature. Compounds **L1**–**L3** and **1**–**5** were authenticated by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS. The single-crystal structures of **1**, **2**, **4**, and **5** were solved. Thermally stable, moisture- and air-insensitive complexes **1**–**5** were found to be efficient catalysts for Suzuki–Miyaura coupling reactions. It appears that Pd complexes **2**, **4**, and **5** catalyze the coupling homogeneously, whereas Pd complexes **1** and **3** are pre-catalysts that generate real catalytic species in situ, which are NPs approximately 2–4 nm in size that contained Pd^0 protected by the ligand or its fragments. The two-phase test carried out by using **1** indicated the homogeneous nature of the catalytic process, which probably occurs through leaching of Pd^0 from these NPs. Palladacycles **1** and **3** are catalytically more active than the four-coordinated complexes **2**, **4**, and **5**. Thus activation of Suzuki coupling with palladium complex varies with the mode of coordination of the ligand. Palladacycles and palladium complexes designed using the same ligand [**L1** and **L2** coordinating as N,C^- and N,O^- ligands, respectively] were found to follow different pathways. Thus a direct comparison of palladacycle with palladium(II) complexes with minimized ligand factors has been presented for the first time, which indicates the superiority of the former on the basis of experiments carried out on palladacycle or palladium(II) complexes alone without accounting for differences in ligands.

Experimental Section

Physical Measurements: ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13 and 75.47 MHz, respectively. The chemical shifts are reported in ppm relative to the internal standard (tetramethylsilane) in the case of both ^1H and $^{13}C\{^1H\}$ NMR spectra. All reactions were carried out in glassware dried in an oven. The diffraction data on single crystals of **1**, **2**, **4**, and **5** were collected using Mo-K_α (0.71073 Å) radiation at 298(2) K. The SADABS[21] software was used for absorption correction (if needed) and SHELXTL for the space group, structure determination, and refinements.[22] Transmission electron microscopic studies were carried out with a JEOL JEM 200CX TEM instrument operated at 200 kV. The specimens for these studies were prepared by dispersing the powdered sample in ethanol by means of ultrasonic treatment. A few drops of the resulting homogenized slurry were put on a porous carbon film supported on a copper grid and dried in air. The elemental composition of NPs was studied with a Carl ZEISS EVO5O scanning electron microscope and an associated QuanTax 200 EDX system, which is based on SDD technology and provides an energy resolution of 127 eV at Mn-K_α. The sample was mounted on a circular metallic sample holder with a sticky carbon tape. High-resolution mass spectral (HRMS) measurements were performed with electrospray ionization (10 eV, 180 °C source temperature) and using sodium formate as calibrant with a Bruker MIcroTOF-Q II and by samples dissolved in CH_3CN.

CCDC-1015573 (for **1**), -1015574 (for **2**), -1015575 (for **4**), and -1015576 (for **5**) 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.

Chemical and Reagents: 2-Hydroxybenzophenone, 2,4-dihydroxybenzophenone, 2-hydroxyacetophenone, 2-thiophenemethylamine, palladium(II) chloride, sodium tetrachloropalladate, and methyl iodide were procured from Sigma–Aldrich (USA) and used as received. 2-Hydroxy-4-methoxybenzophenone was prepared by a previously reported procedure.[13] The solvents were dried and distilled before use by means of standard procedures.[23] The common reagents and chemicals available commercially and domestically were used.

Synthesis of L1, L2, and L3: 2-Thiophenemethylamine (0.565 g, 5.0 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. 2-Hydroxybenzophenone (0.991 g, 5.0 mmol) or 2-hydroxy-4-methoxybenzophenone (1.14 g, 5.0 mmol) or 2-hydroxyacetophenone (0.681 g, 5.0 mmol) dissolved in dry ethanol (20 mL) was added dropwise with stirring. The mixture was stirred further at room temperature for 5 h. The solvent was evaporated with a rotary evaporator to result in **L1** and **L3** as yellow solid and **L2** as yellow oil, respectively.

Ligand L1: Yield: 1.319 g, 90%; m.p. 97 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 4.68 (s, 2 H, H^5), 6.67 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H^{11}), 6.81–6.88 (m, 2 H, H^{12}, H^3), 6.95 (t, $^3J_{H,H}$ = 4.8 Hz, 1 H, H^2), 7.05 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, H^9), 7.20–7.32 (m, 4 H, H^1, H^{10}, H^{15}), 7.52–7.55 (m, 3 H, H^{14}, H^{16}), 15.15 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 50.7 (C^5), 117.6 (C^{11}), 117.8 (C^9), 119.8 (C^7), 124.4 (C^2), 124.5 (C^3), 126.8 (C^1), 127.2 (C^{15}), 128.8 (C^{14}), 129.2 (C^{16}), 131.8 (C^{12}), 132.6 (C^{10}), 133.7 (C^{13}), 141.9 (C^4), 162.6 (C^8), 174.8 (C^6) ppm. HRMS (CH_3CN) [M + H]$^+$: *m/z* calcd. for $[C_{18}H_{16}NOS]^+$ 294.0947; found 294.0956 (Δ = –3.1 ppm). $C_{18}H_{15}NOS$ (293.38): calcd. C 73.69, H 5.15, N 4.77; found C 73.59, H 5.06, N 4.84.

Ligand L2: Yield: 1.487 g, 92%. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 3.81 (s, 3 H, OMe), 4.65 (s, 2 H, H^5), 6.71 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, H^{11}), 6.89 (s, 1 H, H^9), 6.94 (t, $^3J_{H,H}$ = 4.8 Hz, 2 H, H^{12}, H^3), 7.21–7.27 (m, 4 H, H^1, H^2, H^{15}), 7.53–7.58 (m, 3 H, H^{14}, H^{16}), 15.88 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 49.4 (OMe), 55.2 (C^5), 101.6 (C^{11}), 105.8 (C^9), 113.3 (C^7), 124.5 (C^2), 124.6 (C^3), 126.8 (C^1), 127.4 (C^{15}), 128.8 (C^{14}), 129.3 (C^{16}), 129.7 (C^{13}), 133.0 (C^{12}), 141.9 (C^4), 163.7 (C^8), 166.9 (C^{10}), 174.0 (C^6) ppm. HRMS (CH_3CN) [M + H]$^+$: *m/z* calcd. for $[C_{19}H_{18}NO_2S]^+$ 324.1053; found 324.1056 (Δ = –0.9 ppm).

Ligand L3: Yield: 1.041 g, 90%; m.p. 82 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.42 (s, 3 H, H^{13}), 4.95 (s, 2 H, H^5), 6.81 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, H^3),6.94–6.99 (m, 3 H, H^2, H^9, H^{11}), 7.23–7.33 (m, 2 H, H^1, H^{10}), 7.55 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, H^{12}), 15.64 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 14.8 (C^{13}), 48.7 (C^5), 117.5 (C^{11}), 118.5 (C^9), 119.6 (C^7), 124.5 (C^2), 124.7 (C^3), 126.9 (C^1), 128.1 (C^{12}), 132.5 (C^{10}), 141.7 (C^4), 162.9 (C^8), 172.1 (C^6) ppm. HRMS (CH_3CN) [M + H]$^+$: *m/z* calcd. for $[C_{13}H_{14}NOS]^+$ 232.0791; found 232.0794 (Δ = –1.6 ppm). $C_{13}H_{13}NOS$ (231.31): calcd. C 67.50, H 5.66, N 6.06; found C 67.44, H 5.61, N 6.09.

Synthesis of 1 and 3: $[PdCl_2(CH_3CN)_2]$ (0.516 g, 0.2 mmol) was added to a stirred solution of **L1**(0.058 g, 0.2 mmol)/**L2**(0.065 g, 0.2 mmol) in CH_3CN (5 mL) at 70 °C. The reaction mixture was stirred for 5 h, concentrated with a rotary evaporator up to 2 mL, and mixed with diethyl ether (15 mL). The resulting orange compound was filtered, washed with diethyl ether (10 mL), and dried under vacuum to give **1** and **3** as a yellow solid. Single crystals of **1** were grown by slow evaporation of its solution in acetonitrile and methanol (3:1).

Compound 1: Yield: 0.078 g, 82%; m.p. 176 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.01 (s, 3 H, CH_3CN), 4.30 (s, 2 H, H^5), 6.77–6.91 (m, 1 H, H^{11}), 7.42–7.44 (m, 3 H, H^2, H^3, H^9), 7.49–7.55 (m, 4 H, H^1, H^{10}, H^{12}, H^{17}), 7.61–7.68 (m, 3 H, H^{15}, H^{16}, H^{18}), 12.05 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 15.4 (CH_3 of CH_3CN), 43.5, 116.8, 120.7, 125.4, 126.7, 127.5, 128.4, 129.9, 130.8, 131.1, 132.3, 132.5, 133.6, 136.4, 139.2, 147.8, 163.3, 170.6 ppm. HRMS (CH_3CN) [(**L1**)$_2$Pd]$^+$: *m/z* calcd. for $[C^{36}H_{28}N_2O_2PdS_2]^+$ 690.0633; found 690.0628 (Δ = 5.1 ppm). $C_{20}H_{17}ClN_2OPdS$ (475.28): calcd. C 50.54, H 3.61, N 5.89; found C 50.48, H 3.56, N 6.03.

Compound 3: Yield: 0.081 g, 81%; m.p. 145 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.17 (s, 3 H, CH_3CN), 3.96 (s, 3 H, OMe), 4.95 (s, 2 H, H^5), 6.56–6.68 (m, 2 H, H^2, H^{11}), 6.88–6.98 (m, 3 H, H^1, H^3, H^9), 7.14 (s, 2 H, H^{12}, H^{17}), 7.56 (s, 1 H, H^{15}), 7.76 (s, 2 H, H^{16}, H^{18}), 12.68 (s, 1 H, OH) ppm. HRMS (CH_3CN) [(**L2**)$_2$Pd]$^+$: *m/z* calcd. for $[C_{38}H_{33}N_2O_4PdS_2]^+$ 751.0924; found 751.0904 (Δ = 4.2 ppm). $C_{21}H_{19}ClN_2O_2PdS$ (505.31): calcd. C 49.91, H 3.79, N 5.54; found C 49.83, H 3.21, N 5.46.

Synthesis of 2, 4, and 5: Na_2PdCl_4 (0.029 g, 0.1 mmol) was dissolved in water (5.0 mL). A solution of ligand **L1** (0.058 g, 0.2 mmol)/**L2** (0.065 g, 0.2 mmol)/**L3** (0.046 g, 0.2 mmol) in acetone (10 mL) was added with vigorous stirring. The mixture was further stirred for 2 h. The orange-red reaction mixture was extracted with chloroform (25 mL). The chloroform layer was washed with water (100 mL), dried with anhydrous Na_2SO_4, and the solvents evaporated to dryness with rotary evaporator to obtain **2**, **4**, and **5** as an orange powder. Their single crystals were grown from a mixture of $CHCl_3$/hexane (8:2).

Compound 2: Yield: 0.058 g, 85%; m.p. 211 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 5.08 (s, 4 H, H^5), 6.35 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, H^{11}), 6.59 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H^{12}), 6.82–6.90 (m, 6 H, H^2, H^3, H^9), 7.10 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, H^1), 7.18–7.22 (m, 6 H, H^{10}, H^{15}), 7.46–7.50 (m, 6 H, H^{14}, H^{16}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 50.0 (C^5), 114.8 (C^{11}), 121.1 (C^{12}), 125.0 (C^1), 125.4 (C^7), 125.9 (C^3), 126.3 (C^2), 128.0 (C^{15}), 128.6 (C^{16}), 129.1 (C^{14}), 133.5 (C^{10}), 134.5 (C^9), 136.5 (C^{13}), 141.5 (C^4), 165.9 (C^8), 170.5 (C^6) ppm. HRMS (CH_3CN) [M + Na]$^+$: *m/z* calcd. for $[C^{36}H_{28}N_2NaO_2PdS_2]^+$ 713.0531; found 713.0521 (Δ = 3.7 ppm). $C_{36}H_{28}N_2O_2PdS_2$ (691.15): calcd. C 62.56, H 4.08, N 4.05; found C 62.57, H 3.95, N 4.07.

Compound 4: Yield: 0.061 g, 81%; m.p. 206 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 3.68 (s, 6 H, OMe), 4.97 (s, 4 H, H^5), 5.94 (d, $^3J_{H,H}$ = 9.3 Hz, 2 H, H^{11}), 6.22 (s, 2 H, H^{12}), 6.45 (d, 2 H, H^2), 6.87 (s, 4 H, H^3, H^9), 7.15–7.17 (m, 4 H, H^1, H^{15}), 7.45 (s, 4 H, H^{14}, H^{16}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 49.6 (OMe), 55.1 (C^5), 102.2 (C^{11}), 105.1 (C^9), 119.1 (C^7), 124.6 (C^2), 125.5 (C^3), 126.3 (C^1), 127.9 (C^{15}), 128.4 (C^{14}), 128.8 (C^{16}), 135.7 (C^{13}), 136.7 (C^{12}), 142.3 (C^4), 164.0 (C^8), 167.8 (C^{10}), 169.7 (C^6) ppm. HRMS (CH_3CN) [M + H]$^+$: *m/z* calcd. for $[C_{38}H_{33}N_2O_4PdS_2]^+$ 751.0924; found 751.0930 (Δ = –2.4 ppm). $C_{38}H_{32}N_2O_4PdS_2$ (751.20): calcd. C 60.76, H 4.29, N 3.73; found C 60.80, H 4.27, N 3.64.

Compound 5: Yield: 0.047 g, 83%; m.p. 208 °C. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.49 (s, 3 H, H^{13}), 5.29 (s, 2 H, H^5), 6.57 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, H^3), 6.73 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, H^2), 6.95 (t, $^3J_{H,H}$ = 4.8 Hz, 1 H, H^9), 7.04–7.13 (m, 2 H, H^1, H^{11}), 7.22 (d, $^3J_{H,H}$ =

5.1 Hz, 1 H, H^{10}), 7.36 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, H^{12}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, TMS): δ = 19.4 (C^{13}), 49.7 (C^5), 115.3 (C^9), 121.4 (C^{11}), 124.8 (C^1), 125.6 (C^3), 126.6 (C^2), 127.3 (C^7), 130.2 (C^{12}), 132.9 (C^{10}), 140.6 (C^4), 165.5 (C^8),169.3 (C^6) ppm. HRMS (CH_3CN) [M + Na]$^+$: *m/z* calcd. for $[C_{26}H_{24}N_2NaO_2PdS_2]^+$ 589.0215; found 589.0202 (Δ = 3.0 ppm). $C_{26}H_{24}N_2O_2PdS_2$ (567.01): calcd. C 55.07, H 4.27, N 4.94; found C 54.94, H 4.13, N 5.02.

General Procedure for Suzuki–Miyaura Coupling Reaction of Aryl Halides with Phenylboronic Acid: An oven-dried flask was charged with aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), DMF (3.0 mL), H_2O (2.0 mL), and a solution of catalyst **1**–**5** in DMF (100 μL of 10^{-4} M ≡ 10^{-5} mmol or 10^{-3} mol-%; 100 μL of 10^{-3} M ≡ 10^{-4} mmol or 10^{-2} mol-%; 1000 μL of 10^{-3} M ≡ 10^{-3} mmol or 10^{-1} mol-%) was then added with a syringe. The flask was fitted with a water condenser and placed on an oil bath maintained at 90 °C. The reaction mixture was stirred and the reaction monitored with TLC until the conversion of aryl halide to product reached its maximum. Thereafter the mixture was extracted with diethyl ether (2 × 20 mL). The extract was washed with water (50 mL) and dried with anhydrous Na_2SO_4. The solvent of the extract was evaporated with a rotary evaporator, and the residue was purified with a column of silica gel using $CHCl_3$(5%)/hexane as an eluent. All coupling products were authenticated by means of their ^1H and $^{13}C\{^1H\}$ NMR spectra.

Hg Poisoning Test: An excess amount of Hg (Hg/Pd 400:1) was added to a reaction flask before the addition of reactants. Thereafter the coupling reaction of 4-bromobenzaldehyde (1.0 mmol) with phenylboronic acid (1.2 mmol) using **1** or **2** (0.1 mol-%) as a catalyst was carried out in the flask under optimum conditions. A conversion of 94% was observed after 10 h of reaction.

PPh_3 Poisoning Test: PPh_3 (0.5 mol-%) was added under optimum conditions to the coupling reaction of 4-bromobenzaldehyde with phenylboronic acid before addition of catalyst **1** (0.1 mol-%). After 10 h of reaction cross-coupled products were obtained in 95% yield.

Two-Phase Test: 4-Bromobenzoic acid immobilized (as amide) silica (0.20 g) was prepared by following a standard procedure[24] (details in the Supporting Information). Phenylboronic acid (0.36 g, 3 mmol), 4-bromoacetophenone (0.20 g, 1 mmol), and K_2CO_3 (0.56 g, 4 mmol) were taken in a solvent mixture [DMF (8 mL) and water (4 mL)] and heated at 90 °C for 10 h. Thereafter the reaction mixture was cooled to room temperature and filtered through a G-4 crucible. The residue was washed with H_2O (20 mL) followed by diethyl ether (50 mL). The filtrate and washings were collected and mixed with water (50 mL). The resulting aqueous mixture was extracted with diethyl ether (50 mL). The solvent of the extract was evaporated with a rotary evaporator, and the residue was subjected to ^1H NMR spectroscopy. The solid residue was hydrolyzed with KOH [1.68 g dissolved in EtOH (10 mL) and H_2O (5 mL)] at 90 °C for 3 d. The resulting solution was neutralized with aqueous 20% (v/v) HCl, then extracted with dichloromethane, followed by ethyl acetate. The solvent of the combined extract was evaporated, and the resulting residue was analyzed with ^1H NMR spectroscopy.

Isolation of NPs Generated from Complexes 1 and 3 During Suzuki–Miyaura Coupling: A mixture of Pd^{II} complex **1** or **3** (0.5 mmol), phenylboronic acid (1.5 mmol), 4-bromobenzaldehyde (1.0 mmol), and K_2CO_3 (2.0 mmol) in DMF (4.0 mL) and water (4.0 mL) was heated at 90 °C for 10 h and then cooled to room temperature. The solvent was decanted, and the black residue (NPs) was washed with a water/acetone mixture (1:3) and dried under vacuum. The NPs were characterized by means of SEM-EDX and HRTEM.

Procedure for Suzuki–Miyaura Coupling Catalyzed by NPs Obtained from 1 and 3: The coupling reactions of 4-bromobenzaldehyde, 4-bromotoluene, and 4-bromoanisole in the presence of NPs obtained from **1**/**3** (Pd: 1.0 mol-%) were carried out under conditions optimized for complexes **1**/**3**. All products were authenticated by means of ^1H and $^{13}C\{^1H\}$ NMR spectra.

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[1] a) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, Germany, **2004**; b) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, Germany, **1998**; c) *Handbook of Organopalladium Chemistry for Organic Synthesis* (Eds.: E. Negishi, A. de Meijere), Wiley-Interscience, New York, **2002**, p. 1669.

[2] J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527.

[3] a) N. Miyaura, A. Suzuki, in: *Advances in Metal-Organic Chemistry* (Ed.: L. S. Liebeskind), JAI, London, **1998**, vol. 6, p. 187; b) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633.

[4] a) T. J. Colacot, *Platinum Met. Rev.* **2011**, *55*, 84; b) A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722; *Angew. Chem.* **2011**, *123*, 6854; c) A. Suzuki, Y. Yamamoto, *Chem. Lett.* **2011**, *40*, 894; d) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147; e) A. V. Gaikwad, A. Holuigue, M. B. Thathagar, J. E. T. Elshof, G. Rothenberg, *Chem. Eur. J.* **2007**, *13*, 6908.

[5] a) J. P. Wolfe, S. L. Buchwald, *Angew. Chem. Int. Ed.* **1999**, *38*, 2413; *Angew. Chem.* **1999**, *111*, 2570; b) A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 4020; c) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176; *Angew. Chem.* **2002**, *114*, 4350; d) X. Bei, H. W. Turner, W. H. Weinberg, A. S. Guram, *J. Org. Chem.* **1999**, *64*, 6797.

[6] a) R. B. Bedford, C. S. J. Cazin, *Chem. Commun.* **2001**, 1540; b) R. B. Bedford, S. L. Hazelwood, M. E. Limmert, *Chem. Commun.* **2002**, 2610; c) J. Ma, X. Cui, L. Gao, Y. Wu, *Inorg. Chem. Commun.* **2007**, *10*, 762; d) C. A. Fleckenstein, H. Plenio, *Organometallics* **2007**, *26*, 2758; e) S. Teo, Z. Weng, T. S. A. Hor, *Organometallics* **2006**, *25*, 1199; f) J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9550.

[7] a) C. Fleckenstein, S. Roy, S. Leuthaeusser, H. Plenio, *Chem. Commun.* **2007**, 2870; b) A. I. Moncada, J. M. Tanski, L. M. Slaughter, *J. Organomet. Chem.* **2005**, *690*, 6247; c) C. Zhang, M. L. Trudell, *Tetrahedron Lett.* **2000**, *41*, 595; d) K. N. Sharma, H. Joshi, A. K. Sharma, O. Prakash, A. K. Singh, *Organometallics* **2013**, *32*, 2443.

[8] a) Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen, Z. Yang, *Org. Lett.* **2004**, *6*, 3337; b) S. M. Nobre, A. L. Monteiro, *J. Mol. Catal. A* **2009**, *313*, 65.

[9] a) D. Zim, A. S. Gruber, G. Ebeling, J. Dupont, A. L. Monteiro, *Org. Lett.* **2000**, *2*, 2881; b) D. Zim, S. M. Nobre, A. L. Monteiro, *J. Mol. Catal. A* **2008**, *287*, 16; c) V. A. Kozlov, D. V. Aleksanyan, Yu. V. Nelyubina, K. A. Lyssenko, E. I. Gutsul, L. N. Puntus, A. A. Vasil'ev, P. V. Petrovskii, I. L. Odinets, *Organometallics* **2008**, *27*, 4062; d) C. A. Kruithof, A. Berger, H. P. Dijkstra, F. Soulimani, T. Visser, M. Lutz, A. L. Spek,

R. J. M. K. Gebbink, G. V. Koten, *Dalton Trans.* **2009**, 3306; e) V. A. Kozlov, D. V. Aleksanyan, Yu. V. Nelyubina, K. A. Lyssenko, E. I. Gutsul, A. A. Vasil'ev, P. V. Petrovskii, I. L. Odinets, *Dalton Trans.* **2009**, 8657; f) V. A. Kozlov, D. V. Aleksanyan, Yu. V. Nelyubina, K. A. Lyssenko, A. A. Vasil'ev, P. V. Petrovskii, I. L. Odinets, *Organometallics* **2010**, *29*, 2054; g) D. V. Aleksanyan, V. A. Kozlov, Y. V. Nelyubina, K. A. Lyssenko, L. N. Puntus, E. I. Gutsul, N. E. Shepel, A. A. Vasil'ev, P. V. Petrovskii, I. L. Odinets, *Dalton Trans.* **2011**, *40*, 1535.

[10] a) K. N. Sharma, H. Joshi, V. V. Singh, P. Singh, A. K. Singh, *Dalton Trans.* **2013**, *42*, 3908; b) H. Joshi, K. N. Sharma, A. K. Sharma, A. K. Singh, *Nanoscale* **2014**, *6*, 4588.

[11] G. C. Fortman, S. P. Nolan, *Chem. Soc. Rev.* **2011**, *40*, 5151.

[12] a) A. Panda, *Coord. Chem. Rev.* **2009**, *253*, 1056; b) G. K. Rao, A. Kumar, B. Kumar, D. Kumar, A. K. Singh, *Dalton Trans.* **2012**, *41*, 1931; c) A. Kumar, G. K. Rao, S. Kumar, A. K. Singh, *Dalton Trans.* **2013**, *42*, 5200; d) A. Kumar, G. K. Rao, F. Saleem, A. K. Singh, *Dalton Trans.* **2012**, *41*, 11949.

[13] G. K. Rao, A. Kumar, S. Kumar, U. B. Dupare, A. K. Singh, *Organometallics* **2013**, *32*, 2452.

[14] A. Kumar, M. Agarwal, A. K. Singh, *Inorg. Chim. Acta* **2009**, *362*, 3208.

[15] J. Tsuji, *Palladium Reagents and Catalysts, New Perspectives for the 21st Century*, Wiley, Chichester, UK, 1st ed. **2004**.

[16] a) C. R. LeBlond, A. T. Andrews, Y. Sun, J. R. Sowa, *Org. Lett.* **2001**, *3*, 1555; b) Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Commun.* **2007**, 5069.

[17] a) A. Arcadi, G. Cerichelli, M. Chiarini, M. Correa, D. Zorzan, *Eur. J. Org. Chem.* **2003**, 4080; b) M. Lysen, K. Kohler, *Synthesis* **2006**, 692.

[18] A. Kumar, G. K. Rao, S. Kumar, A. K. Singh, *Organometallics* **2014**, *33*, 2921.

[19] J. Rebek, F. Gavina, *J. Am. Chem. Soc.* **1975**, *97*, 454.

[20] J. Hu, Y. B. Liu, *Langmuir* **2005**, *21*, 2121.

[21] G. M. Sheldrick, *SADABS*, v. 2.10, University of Göttingen, Germany, **2003**.

[22] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 467; b) G. M. Sheldrick, *SHELXL-NT*, v. 6.12, University of Göttingen, Germany, **2000**.

[23] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., ELBS, Longman Group, Harlow, UK, **1989**.

[24] J. D. Webb, S. MacQuarrie, K. McEleney, C. M. Crudden, *J. Catal.* **2007**, *252*, 97.

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Pd-Catalyzed Coupling Reactions

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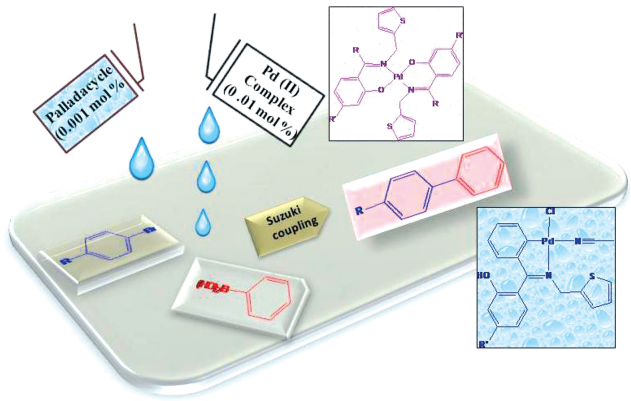

Catalysis of Suzuki coupling reactions with palladacycles (≥ 0.001 mol-%) and palladium complexes (≥ 0.01 mol-%) proceeds with and without nanoparticles.

