

Bidentate [C,N] Schiff base ligand palladacycles: Synthesis, X-ray diffractometric analysis and survey of their catalytic activity

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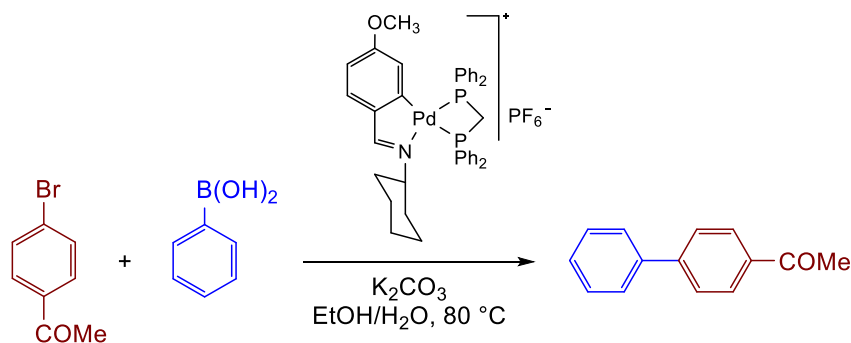
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Abstract

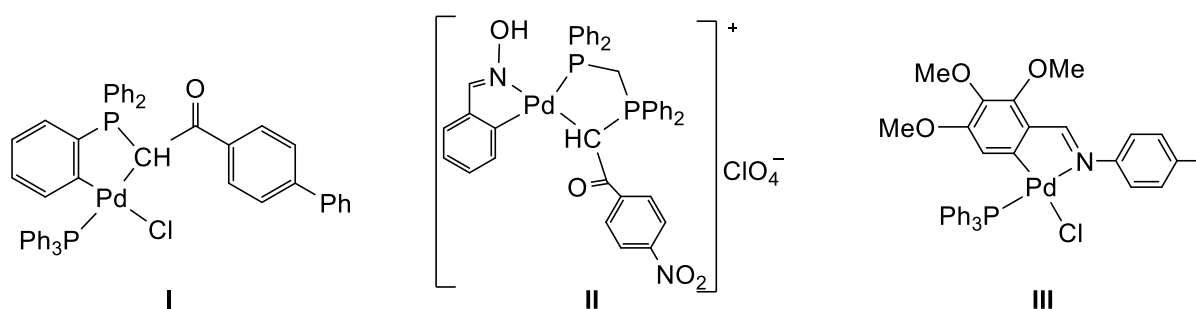
Palladacycles have been synthesized from Pd(OAc)₂ and Schiff base ligands via C-H activation, to render dinuclear acetate-bridged compounds. The latter are starting materials for the sequence of reactions leading to the ensuing complexes. Treatment of the μ -acetate dinuclear complexes with aqueous sodium chloride in a typical metathesis reaction, gave the corresponding μ -chloride dinuclear complexes. Reaction of the latter with triphenylphosphine or with bis(diphenylphosphino)methane (dppm) in a 1:2 ratio, and ammonium hexafluorophosphate, gave the single nuclear complexes in a bridge-splitting reaction. The compounds were characterized by microanalysis (CHN), IR and ¹H and ³¹P{¹H} NMR spectroscopy. The crystal structures of two of them were determined by single-crystal X-ray diffraction. Additionally, the performance of the synthesized palladacycles as catalysts has been evaluated in the Suzuki-Miyaura cross-coupling reaction: they are suitable for the cross coupling of a rather large number of substrates in high yields under mild conditions.



Keywords: Cyclometallated, palladium, Schiff base, phosphine, X-ray study.

Introduction

The chemistry of cyclometallated transition metal complexes has attracted much attention in past years since the first example appeared,¹ with those possessing five-membered metallated rings receiving the most in-depth study. Numerous accounts have been undertaken regarding cyclopalladation reactions, inclusive of preparative techniques, reactivity patterns with a wide range of nucleophiles, and structural features especially in the particular case of the palladacycles bearing nitrogen donor ligands.²⁻⁵ Palladacycle complexes with bidentate [C,N] ligands are efficient tools in catalytic methods in organic synthesis, in which novel palladacycles have shown their paramount role for the preparations;⁶ Milstein *et al.* have developed a wide variety of imine-based palladacycles for the cross-coupling processes.⁷ One of the most significant and often used methods for creating carbon-carbon bonds is the Suzuki-Miyaura cross-coupling reaction.^{8,9} Although many palladium-mediated coupling reactions involve palladacycle intermediates,¹⁰⁻¹⁴ commercially available reagent such as $[Pd(OAc)_2]$ and $[Pd(Ph_3P)_4]$ are more than acceptable catalysts; nevertheless, the palladacycles have appeared as an important class of catalysts due in part to their air and water stability. Hermann *et al.* achieved for the first time palladacycles having a phosphorus donor atom on the metallacycle, as catalysts for the Heck and Suzuki reactions and since then many new species have been reported.^{15,16} The catalytic activity of other palladacycles containing phosphine as well as halide ligands have also been investigated in the Suzuki cross-coupling. The former show a rather strong donor capability and π accepting capability.¹⁷⁻²²



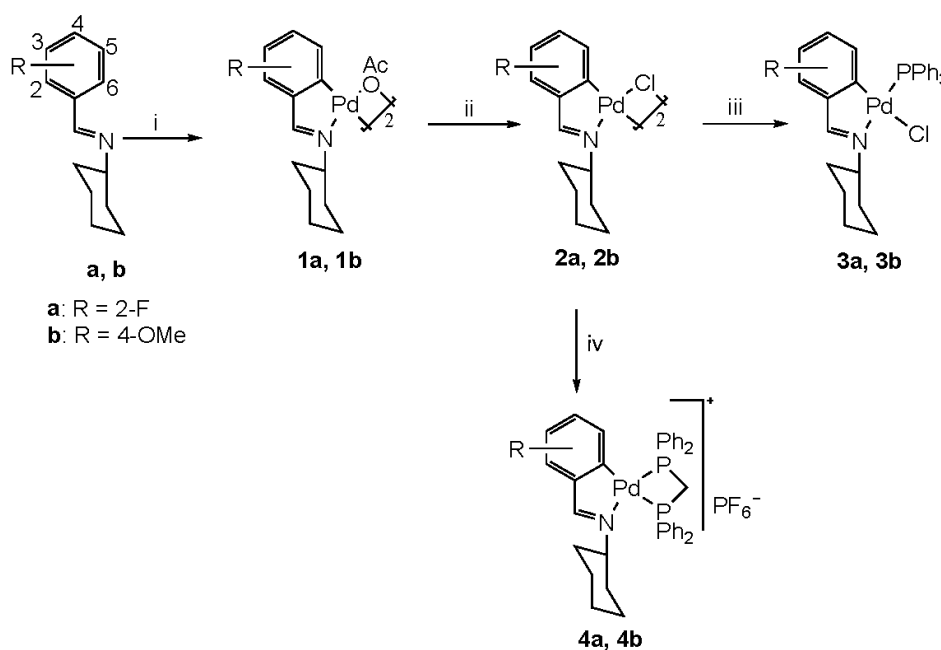
Scheme 1. Palladacycles active as catalysts in the Suzuki cross-coupling reaction.

In previous studies, we demonstrated that functionalized imine palladacycles gave good yields in Suzuki-Miyaura coupling by modifying the reaction conditions, such as the base, time, and temperature, due to their greater simplicity in synthesis and stability.²³ Herein, we describe the synthesis and characterization of single and dinuclear palladacycles which have been tested as catalysts for the Suzuki-Miyaura cross-coupling. The compounds were characterized by microanalytical data (C, H, N), and by IR and 1H -NMR, ^{31}P - $\{^1H\}$ NMR spectroscopies. Two compounds, **3a** and **4b**, were also studied by X-Ray diffraction analysis. In the Suzuki cross-coupling reaction, we investigated the catalytic activity of palladacycle compounds.

Results and Discussion

For the convenience of the reader, the compounds and reactions are shown in Scheme 2. Chloroform solutions containing equimolar quantities of the corresponding aldehyde and amine were heated at reflux to give the imine ligands **a** and **b** in high yield *ca.* 95%. The NMR data for these ligands agreed with that in the

literature. Reaction of **a** or **b** with Pd(OAc)₂ yielded dinuclear cyclopalladated compounds with acetate-bridging ligands **1a** and **1b**, respectively, with the ligand bonded to palladium(II) *via* the deprotonated benzylidene *ortho* carbon atom and the nitrogen atom from the C=N double bond. In the IR spectra, the $\nu(\text{C}=\text{N})$ stretching vibration was shifted to lower wavenumbers in agreement with coordination of the metal *via* the nitrogen lone pair (1629 and 1643 cm⁻¹).²⁴ The bridging coordination mode of the acetate ligands was confirmed by the separation of the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ vibrations in the IR spectra *ca.* 160 cm⁻¹.²⁵ In the ¹H NMR spectra, the HC=N proton resonance was high field shifted *ca.* 0.9-1 ppm based on its position in the free ligand spectrum;²⁴ furthermore, absence of the C(6)-H resonance in the ¹H NMR spectra was indicative of metalation at the C(6) site. Treatment of compounds **1a** and **1b** with aqueous sodium chloride gave cyclopalladated compounds **2a** and **2b**, respectively, with chloride-bridging ligands (see Experimental). The IR spectra showed two $\nu(\text{Pd}-\text{Cl})$ bands for each complex assigned to the $\nu(\text{Pd}-\text{Cl})_{\text{transN}}$, (348, 320 cm⁻¹) and $\nu(\text{Pd}-\text{Cl})_{\text{transC}}$ (287, 262 cm⁻¹) stretches due to the differing *trans* influence of the phenyl carbon atom and the nitrogen atom, confirming an asymmetric nature of the Pd₂Cl₂ bridging unit, and the ¹H NMR spectra confirmed the absence of the acetate ligand resonances. Single nuclear compounds were obtained by bridge-splitting reactions with monodentate (Ph₃P) and bidentate (Ph₂PCH₂PPh₂, dppe) phosphine ligands, **3a**, **3b** and **4a**, **4b**, respectively.



Scheme 2. i) Pd(OAc)₂, toluene, reflux; ii) NaCl (aq), acetone, 2 h; iii) Ph₃P, acetone, 3 h; iv) dppe, acetone, 3 h.

The signals for the HC=N protons were a broad singlet for compound **4a** and a doublet for the other compounds, indicating phosphorus nuclei coupling. The ³¹P-{¹H} NMR spectra showed singlet, **3a**, **3b**, and doublet, **4a**, **4b**, resonances; in the latter case suggesting non-equivalent phosphorus nuclei. The assignment of the doublets was made on the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency.²⁶ The singlet signal of the C(4)-OMe resonance was shifted to lower field from the starting product by 0.9/0.5 ppm due to the shielding effect of the phosphine phenyl rings. The HC=N and H5 resonances showed coupling to the phosphorus nucleus *trans* to nitrogen singlets, **3a**, **3b**, and doublet of doublets, **4a**, **4b**, the latter also coupled to the C(4)-H proton.

X-Ray diffraction study

Crystals of **3a** and **4b** were grown by slowly diffusing *n*-hexane into a dichloromethane solution of the corresponding compound. Figures 2 and 4 illustrate the molecular structures of **3a** and **4b**, respectively. The structure of **3a** consists of two molecules per asymmetric unit in **3a**, and two molecules and a hexafluorophosphate anion in the asymmetric unit of **4b**. Each structure consists of a palladium(II) atom bonded in a slightly distorted square-planar arrangement, in **3a** to four different donors, a bidentate imine ligand through the aryl C(1) carbon, the imine nitrogen(1), the chloride ligand Cl(1) and the phosphorus atom P(1) of the triphenylphosphine; in **4b** to a second phosphorus atom from the diphosphine ligand in place of the chloride Cl(1). The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, in the range 97.85(5) to 81.3(2)°, with the distortions being most noticeable in C(1)-Pd(1)-N(1) angle consequent upon chelation of the Schiff base ligand. All bond distances are within the expected range,^{27,28} with allowance for the strong *trans* influence of the phosphorus donor ligand, which is reflected in the Pd(1)-N(1) bond distances [2.110(6) Å], **3a**; [2.118(6) Å], **4b**, which are longer than the signal bond expected value, consequent on the *trans* influence of the phosphine ligand;^{26,27} [cf. sum of the covalent radii for palladium and nitrogen, 2.01 Å].²⁹ The Pd(1)-C(1) bond lengths are essentially equal, [2.034(9) Å], **3a**; [2.033(6) Å], **4b**, [2.033(5) Å] and shorter than the expected value of 2.081 Å; partial multiple-bond character has been invoked as a reasoning.^{30,31} At palladium, the sums of angles are roughly 360°, with angles between adjacent atoms close to the anticipated value of 90°, with distortions more obvious in the somewhat diminished "bite" angles C(1)-Pd(1)-N(1) due to chelation [81.12(3)°, **3a**; 81.21(2)°, **4b**]. The bond angles for **4b** are forced by the steric requirements of the phosphine four-membered chelate ring, P(1)-Pd(1)-P(2) 71.79(6)°. The Pd(1)-P(1) bond distance [2.260(2) Å], **3a**, which is smaller than the sum of the single-bond radii for palladium and phosphorus, 2.41 Å, suggests partial double bond between the two atoms.^{30,31} In compound **4b** the Pd-P distances *trans* to nitrogen Pd(1)-P(1), and *trans* to carbon Pd(1)-P(2) [2.245(16) Å vs 2.377(16) Å], reflect as well the differing *trans* influence of the phenyl carbon atom and the imine nitrogen atom.³² Intermolecular self-assembly between the molecules is established by hydrogen bonds comprising the fluorine atoms and the phenyl protons [C(16)-H(16)⋯F(1) 2.447, C(50)-H(50)⋯F(2) 2.550 Å, C(16)-H(16)⋯F(1) 108.58, C(50)-H(50)⋯F(2) 121.28°]; as well as interactions containing the chlorine atoms and the phenyl protons [C(61)-H(61)⋯Cl(1) 2.847, C(17)-H(17)⋯Cl(2) 2.886 Å, C(61)-H(61)⋯Cl(1) 128.01, C(17)-H(17)⋯Cl(2) 129.11°].

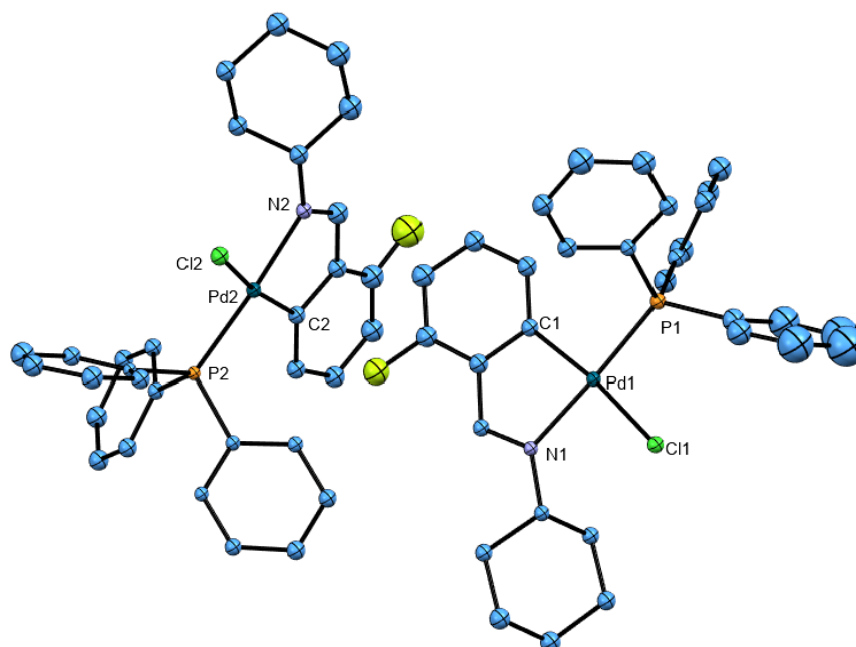


Figure 1. Thermal ellipsoid plot for **3a** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)-C(1) 2.023(8), Pd(1)-N(1) 2.118(6), Pd(1)-Cl(1) 2.364(18), Pd(1)-P(1) 2.260(2), C(1)-Pd(1)-N(1) 81.9(3), N(1)-Pd(1)-Cl(1) 93.11(17), Cl(1)-Pd(1)-P(1) 90.32(7), C(1)-Pd(1)-P(1) 94.7(2), C(1)-Pd(1)-Cl(1) 171.5(2), N(1)-Pd(1)-P(1) 176.50(18). Pd(2)-C(2) 2.017(7), Pd(2)-N(2) 2.110(6), Pd(2)-Cl(2) 2.366(19), Pd(2)-P(2) 2.264(19), C(2)-Pd(2)-N(2) 81.5(3), N(2)-Pd(2)-Cl(2) 91.83(18), Cl(2)-Pd(2)-P(2) 91.97(7), C(2)-Pd(2)-P(2) 95.4(2), C(2)-Pd(2)-Cl(2) 170.2(2), N(2)-Pd(2)-P(2) 173.17(17).

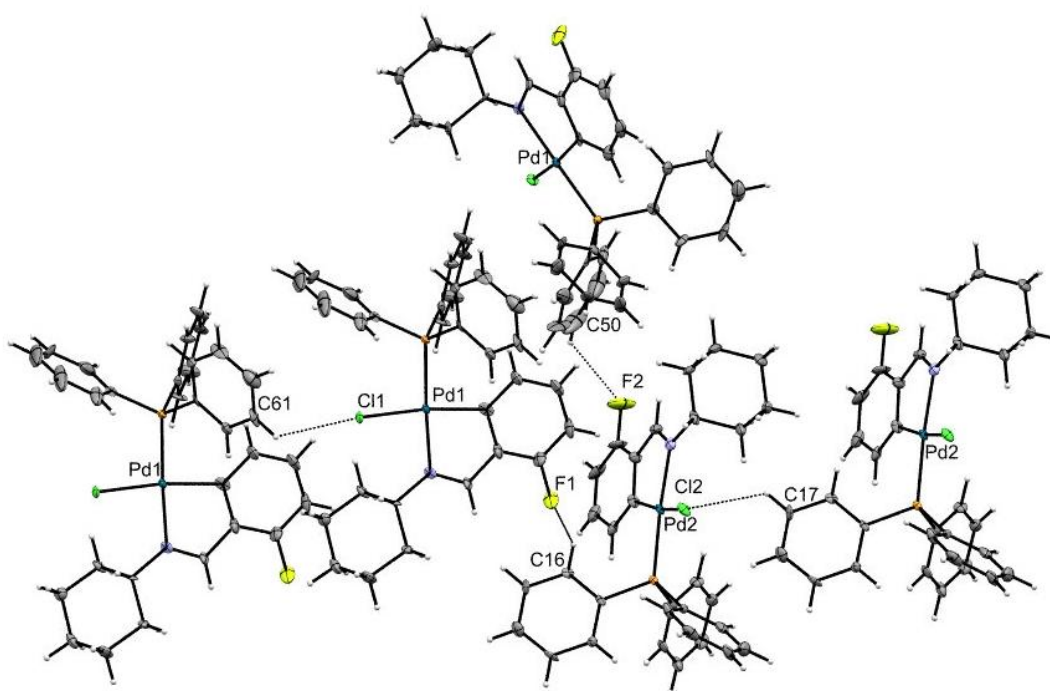


Figure 2. Intermolecular weak interaction in the crystal structure **3a**.

In the crystal structure of **4b** hydrogen bonds are settled between the phenyl protons and the oxygen

atom of the methoxy group displaying a one dimensional polymer along the *c* axis [C(11)-H(11a)⋯O(1) 2.619, C(49)-H(49a)⋯O(2) 2.615 Å, C(11)-H(11a)⋯O(1) 146.14, C(49)-H(49a)⋯O(2) 150.94°].

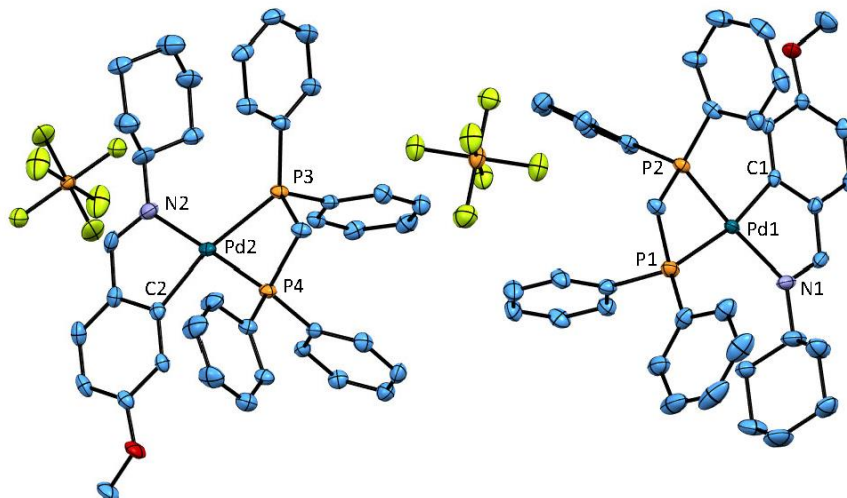


Figure 3. Thermal ellipsoid plot for **4b** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)-C(1) 2.034(5), Pd(1)-N(1) 2.115(4), Pd(1)-P(1) 2.245(12), Pd(1)-P(2) 2.376(12), C(1)-Pd(1)-N(1) 81.25(3), N(1)-Pd(1)-P(1) 177.90(12), P(1)-Pd(1)-P(2) 78.78(4), C(1)-Pd(1)-P(1) 97.83(14), C(1)-Pd(1)-P(2) 167.85(13), N(1)-Pd(1)-P(1) 177.90(12). Pd(2)-C(2) 2.036(4), Pd(2)-N(2) 2.125(4), Pd(2)-P(3) 2.388(13), Pd(2)-P(4) 2.240(12), C(2)-Pd(2)-N(2) 81.10(17), N(2)-Pd(2)-P(3) 110.24(12), P(3)-Pd(2)-P(4) 71.89(4), C(2)-Pd(2)-P(4) 97.06(12), C(2)-Pd(2)-P(3) 168.43(12), N(2)-Pd(2)-P(4) 173.97(15).

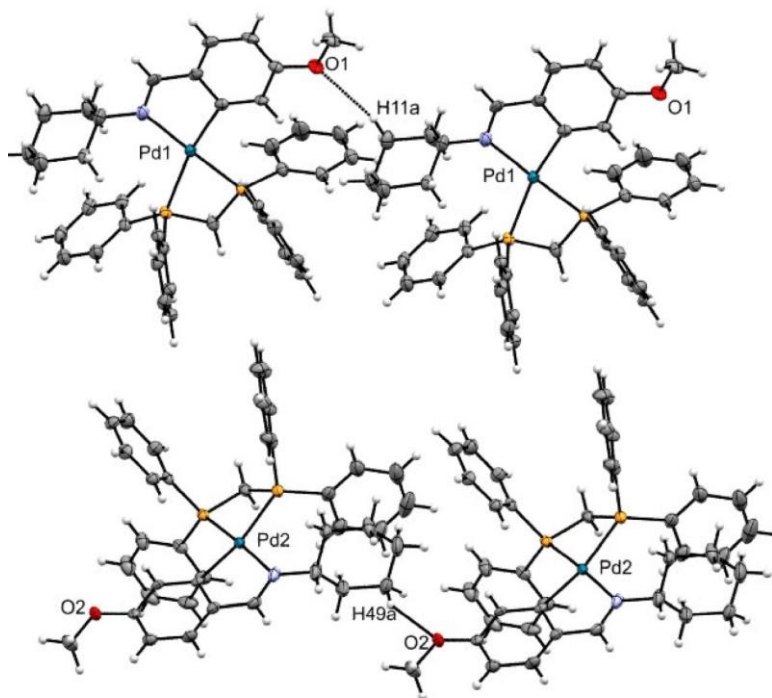
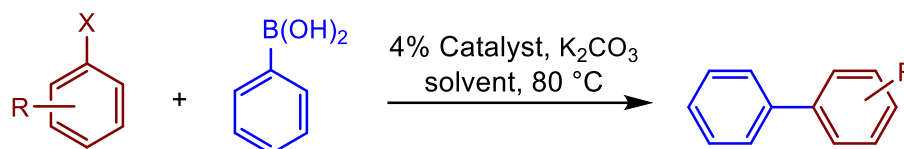


Figure 4. Intermolecular hydrogen weak interactions in the crystal structure of **4b**. solvent molecules and PF₆ ions have been omitted for clarity.

Catalytic activity

To investigate the catalytic activity of the new Schiff base palladacycles described in this work they were used as catalysts in the Suzuki-Miyaura reaction. Thus, treatment of 4-bromoacetophenone with phenylboronic acid in THF/water (2:1) or EtOH/water (2:1) at rt or at 80 °C for a maximum of 24 h in the presence of 2 mol % catalyst and K₂CO₃ as base, gave the biaryl product 4-phenylacetophenone in high yield in all cases (Table 1).

Table 1. The catalytic activity of the compounds in the Suzuki-Miyaura reaction



Entry	[cat.]	Aryl Halide	Product	Solvent ^{a,b}	Time (h)	Yield (%)
1	Pd(OAc) ₂			THF/H ₂ O	24	64
2	1a			THF/H ₂ O	24	>99
3	1b			THF/H ₂ O	24	98
4	2a			THF/H ₂ O	24	95
5	2b			THF/H ₂ O	24	87
6	3a			THF/H ₂ O	24	>90
7	3b			THF/H ₂ O	24	>90
8	4a			EtOH/H ₂ O	17	>85
9	4b			EtOH/H ₂ O	17	>85
10	1a			THF/H ₂ O	24	100
11	3b			THF/H ₂ O	24	100
12	1a			THF/H ₂ O	24	25
13	2b			THF/H ₂ O	24	25
14	3a			THF/H ₂ O	24	>90
15	4a			THF/H ₂ O	24	>90

Table 1. Continued

Entry	[cat.]	Aryl Halide	Product	Solvent ^{a,b}	Time (h)	Yield (%)
16	1a			THF/H ₂ O	24	>90
17	2b			THF/H ₂ O	24	>90
18	3a			THF/H ₂ O	24	85
19	4a			THF/H ₂ O	24	88
20	1a			THF/H ₂ O	24	80
21	2b			THF/H ₂ O	24	88
22	3a			THF/H ₂ O	24	88
23	4a			THF/H ₂ O	24	83

Reaction conditions: Bromoarene (0.1 mmol), phenylboronic acid (1.2 equiv.), K₂CO₃ (2 equiv.), catalyst (4 mol %), 6 mL: ^a THF/H₂O (2:1), ^b EtOH/H₂O (2:1). Temperature, 80 °C.

Hence, under the conditions in Table 1 the cross couplings for 4-bromoacetophenone with phenylboronic acid in aqueous THF or EtOH were satisfactory. It can be seen that the acetate-bridged compounds gave the best conversions, with the exception of the substrates bearing a *p*-substituted formyl group, entry **12**; a similar situation was produced with the bromide-bridged dinuclear compound, entry **13**. This inconvenience was overcome when using phosphine or diphosphine derivatives, giving yields > 90%, entries **14** and **15**. Notwithstanding, with the *o*-substituted formyl moiety all compounds tested gave yields *ca.* 90% or greater, entries **16-19**. Comparison of the results using the complexes with Ph₃P or chelating dppm are much the same, albeit in complexes with the diphosphine quite high yields were obtained using a significantly shorter reaction time, entries **8** and **9**. Nevertheless, the coupling reaction with the present complexes as catalysts was compared with Pd(OAc)₂, entry **1**, under analogous conditions. The results (Table 1) indicate better conversions for all the compounds tested than Pd(OAc)₂, per palladium atom used. Attempts to use Pd(Ph₃P)₄ did not give yields greater than for Pd(OAc)₂. Future research will deal with narrowing the gap between the possible catalysts with application of those chosen in analogous processes in the hope of producing the most suitable palladacycles for such a purpose.

Conclusions

Herein, we have shown that reaction of the corresponding imine ligands with Pd(OAc)₂ produces double nuclear Schiff base palladacycles with bridging acetate ligands, [Pd(C_{sp2},N-imine)(μ-OAc)]₂. The latter complexes are the starting point for the synthesis of the ensuing species. Thus, by a metathesis reaction of the μ-acetate palladacycles the corresponding μ-chloride analogues, [Pd(C_{sp2},N-imine)(μ-Cl)]₂, are easily obtained. Treatment of the latter in a bridge-splitting reaction with mono- or bidentate tertiary phosphines, Ph₃P and dpmm, respectively, renders the single nuclear complexes [PdCl(C_{sp2},N-imine)(PR₃)] and [Pd(C_{sp2},N-imine)(Ph₂PCH₂PPh₂-P,P)(PF₆)]. The molecular structures of **3a** and **4b** have been identified by single-crystal X-ray diffraction; both display intermolecular contacts. All the compounds were applied to the Suzuki-Miyaura cross coupling reaction between a phenylboronic acid and a conveniently substituted aryl bromide in either aqueous THF or EtOH. The compounds tested gave good conversions, showing greater catalytic activity than Pd(OAc)₂ under analogous conditions, ensuring a bright future for these species as potential organic solvent-free catalysts towards a fully green cross coupling process.

Experimental Section

General procedures. Solvents were purified by standard methods.³³ The reactions were carried out under dry nitrogen. Palladium(II) acetate, 4-methoxy-, 2-fluorobenzaldehydes 2-methylthioaniline, triphenylphosphine (Ph₃P) and bis(diphenylphosphino)methane (Ph₂PCH₂PPh₂, dpmm) were purchased from commercial sources. Compounds **a**³⁴ and **b**³⁵ have been previously reported. Elemental analyses were performed with a Thermo Finnigan elemental analysis, model Flash 1112. IR spectra were recorded on Jasco model FT/IR-4600 spectrophotometer. ¹H NMR and spectra in solution were recorded in acetone-*d*₆ or CDCl₃ at rt on Varian Inova 400 spectrometers operating at 400 MHz using 5 mm o.d. tubes; chemical shifts, in ppm, are reported downfield relative to TMS using the solvent signal as reference (acetone-*d*₆ δ_H 2.05, CDCl₃ δ_H 7.26). Similarly, ¹³C NMR {¹H} spectra were recorded at 100 MHz on a Bruker AMX 400 spectrometer. ³¹P NMR spectra in solution were recorded in acetone-*d*₆ or CDCl₃ at rt on Varian Inova 400 spectrometer operating at 162 MHz using 5 mm o.d. tubes and are reported in ppm relative to external H₃PO₄ (85%). Coupling constants are reported in Hz. All chemical shifts are reported downfield from standards. The ESI mass spectra were recorded using a QSTAR Elite mass spectrometer, using acetonitrile or dichloromethane/ethanol as solvents.

N-Cyclohexyl-1-(2-fluorophenyl)methanimine (a). 2-Fluorobenzaldehyde (500 mg, 4.02 mmol) and cyclohexylamine (39 mg, 4.02 mmol) were added in chloroform (40 mL). The mixture, fitted to a Dean-Stark, was heated at reflux for 8 h. The solvent was then removed under vacuum to afford the title compound **a** (793.4 mg, 96%) as a brown oil. IR: ν(C=N) 1629 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_H 8.64 (s, 1H, HC=N), 8.01 (t, ³J(H6H5) = 7.7 Hz, 1H, H6), 7.38 (t, ³J(H3F) = 6.6 Hz, 1H, H3), 7.17 (t, ³J(H5H6) = 7.7, 1H, H5), 7.10-7.00 (m, 1H, H4) 3.40-3.20 (m, 1H, N-CH-Cy), 2.02-1.14 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_C 163.1 (C2); 158.5 (C=N); 122.3 (C1); 116.2 (C3); 135.1 (C4); 125.3 (C5); 130.4 (C6); 73.0 (CH-N); 31-25 (CH₂). Anal. calcd for C₁₃H₁₆FN (205.13): C, 76.1; H, 7.9; N, 6.8. Found: C, 76.0; H, 7.8; N, 6.8%. ESI-MS: *m/z* = 204 (LH)⁺.

N-Cyclohexyl-1-(4-methoxyphenyl)methanimine (b). Prepared similarly to compound **a**. Yellow liquid (757.6 mg, 95%). IR: ν(C=N) 1943 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_H 8.26 (s, 1H, HC=N), 7.68 (d, *J* = 8.3 Hz, 2H, H2, H6), 6.92 (d, *J* = 8.3 Hz, 2H, H3, H5), 3.84 (s, 3H, OMe), 3.30-3.10 (m, 1H, N-CH-Cy), 1.89–1.17 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_C 162.5 (C=N), 161.8 (C4), 130.6 (C1, C6), 117.1 (C3, C5), 135.1 (C4), 74.0

(CH-N), 29.2-25.7 (CH₂). Anal. calcd for C₁₄H₁₉NO (217.15): C, 77.4; H, 8.8; N, 6.5. Found: C, 77.3; H, 8.8; N, 6.4%. ESI-MS: $m/z = 216$ (LH)⁺.

Di- μ -acetate-bis(*N*-cyclohexyl-1-(2-fluorophenyl)methaniminato-C6,*N*)dipalladium(II) (1a). Ligand **a** (700 mg, 5.64 mmol) and Pd(OAc)₂ (1.27 mg, 5.64 mmol) were added in toluene (40 mL). The mixture was stirred for 3 h at 65 °C under argon, and then filtered to remove the trace amount of black palladium formed. The solvent was removed under vacuum, and the residue was recrystallized, washed with cold ethanol, and filtered to give the title compound **1a** (732 mg, 35%) as a yellow solid, mp 204-206 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1615, $\nu_{\text{as}}(\text{COO})$ 1574, $\nu_{\text{s}}(\text{COO})$ 1408 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 7.68 (s, 1H, HC=N), 7.03 (d, ³J(H3F) = 6.5 Hz, 1H, H3), 6.92 (br s, 1H, H5), 6.80-6.60 (m, H4), 3.20-2.90 (m, 1H, N-CH-Cy), 2.15 (s, 3H, OAc), 2.50-0.80 (m, 10H, Cy). ¹³C{¹H} NMR (100 M Hz, acetone-*d*₆) δ_{C} 181.7 (COO), 168.2 (C=N), 164.7 (C2), 159.8 (C6), 151.6 (C1), 132.2 (C5), 135.9 (C4), 128.2 (C3), 71.4 (CH-N), 32-24 (CH₂), 24.3 (CH₃). Anal. calcd for C₃₀H₃₈F₂N₂O₄Pd₂ (741.48): C, 48.6; H, 5.2; N, 3.8. Found: C, 48.4; H, 5.1; N, 3.8%. ESI-MS: $m/z = 740$ ((LH)Pd(OAc))₂⁺.

Di- μ -acetate-bis(*N*-cyclohexyl-1-(4-methoxyphenyl)methaniminato-C6,*N*)dipalladium(II) (1b). Prepared similarly to compound **1a**. Yellow solid, (846 mg, 43%), mp 193-195 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1609, $\nu_{\text{as}}(\text{COO})$ 1570, $\nu_{\text{s}}(\text{COO})$ 1414 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 7.25 (s, 1H, HC=N), 7.00 (d, ³J(H2H3) = 8.2 Hz, 1H, H2), 6.60 (s, 1H, H5), 6.49 (dd, ³J(H3H2) = 8.2 Hz, ⁴J(H3H5) = 3.2 Hz, 1H, H3), 3.79 (s, 3H, OMe), 3.10-2.80 (m, 1H, N-CH-Cy), 2.14 (s, 3H, OAc), 2.50-0.70 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_{C} 184.6 (COO), 170.5 (C=N), 162.0 (C4), 159.8 (C6), 151.6 (C1), 127.3 (C2), 134.6 (C5), 128.2 (C3), 72.3 (CH-N), 31-25 (CH₂), 25.0 (CH₃). Anal. calcd for C₃₂H₄₄N₂O₆Pd₂ (765.55): C, 50.2; H, 5.8; N, 3.7. Found: C, 50.1; H, 5.8; N, 3.6%. ESI-MS: $m/z = 764$ ((LH)Pd(OAc))₂⁺.

Di- μ -chloro-bis(*N*-cyclohexyl-1-(2-fluorophenyl)methaniminato-C6,*N*)dipalladium(II) (2a). Compound **1a** (500 mg) in acetone (15 mL) was treated with 0.05 M aqueous sodium chloride (25 mL). After stirring for 2 h a solid precipitated, which was filtered off, washed with water, and vacuum dried to give the title compound **2a** (215 mg, 45%) as a yellow solid, mp 250-252 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1615, $\nu(\text{Pd}-\text{Cl}_{\text{trans-N}})$ 348, $\nu(\text{Pd}-\text{Cl}_{\text{trans-C}})$ 287 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 8.12 (s, 2H, HC=N), 7.18 (br s, 1H, H3), 7.05 (br s, 1H, H5), 6.70-6.50 (m, 1H, H4), 3.80-3.60 (m, 1H, N-CH-Cy), 1.27-2.25 (m, 10H, Cy). Anal. calcd for C₂₇H₃₃Cl₂F₂N₂Pd₂ (707.31): C, 45.9; H, 4.7; N, 4.0. Found: C, 45.9; H, 4.6; N, 4.0%. ESI-MS: $m/z = 706$ ((LH)Pd(Cl))₂⁺.

Di- μ -chloro-bis(*N*-cyclohexyl-1-(4-methoxyphenyl)methaniminato-C6,*N*)dipalladium(II) (2b). Prepared similarly to compound **2a**. Pale yellow solid, (220 mg, 46%), mp 236-238 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1600, $\nu(\text{Pd}-\text{Cl}_{\text{trans-N}})$ 320, $\nu(\text{Pd}-\text{Cl}_{\text{trans-C}})$ 262 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 7.74 (s, 1H, HC=N), 7.12 (d, ³J(H2H3) = 8.5 Hz, 1H, H2), 6.97 (s, 1H, H5), 6.57 (d, ³J(H3H2) = 8.5 Hz, 1H, H3), 3.83 (s, 3H, OMe), 3.75-3.5 (m, 1H, N-CH-Cy), 2.23-1.21 (m, 10H, Cy). Anal. calcd for C₂₉H₃₉Cl₂O₂N₂Pd₂ (731.38): C, 47.6; H, 5.4; N, 3.8. Found: C, 47.5; H, 5.3; N, 3.8%. ESI-MS: $m/z = 730$ ((LH)Pd(Cl))₂⁺.

{{(N-Cyclohexyl-1-(2-fluorophenyl)methaniminato-C6,*N*)(chloride)(triphenylphosphine)}palladium(II) (3a). Compound **2a** (25 mg, 0.036 mmol) and Ph₃P (18.9, 0.072 mmol) were added in acetone (15 mL) and the mixture was stirred for 3 h at rt. The yellow precipitate formed was filtered off, dried in vacuum, and recrystallized to give the title compound **3a** (27 mg, 62%) as a transparent crystalline solid, mp 178-180 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1589, $\nu(\text{Pd}-\text{Cl})$ 305 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 8.49 (d, ⁴J(PHi) = 8.6 Hz, 1H, Hi), 7.84-7.67 (m, 6H, *o*-PPH), 7.49-7.32 (m, 9H, *p*-, *m*-PPH), 6.65-6.50 (m, 2H, H3, H4), 6.16 (dd, ⁴J(H5P) = 6.0 Hz, ⁴J(H5H3) = 2.3 Hz, 1H, H5), 4.54 (t, ³J(HH) = 11.2 Hz, 1H, N-CH-Cy), 2.30-0.87 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_{C} 166.3 (C=N), 163.7 (C2), 157.8 (C6), 154.7 (C1), 134.4 (C5), 133.9 (C4), 128.2 (C3), 70.6 (CH-N), 33-25 (CH₂). ³¹P NMR (162 MHz, CDCl₃) δ_{P} 42.90s. Anal. calcd for C₃₁H₃₀ClFNPd (608.43): C, 61.2; H, 5.0; N, 2.3. Found: C, 61.1; H, 4.9; N, 2.3%. ESI-MS: $m/z = 607$ ((LH)Pd)(Cl)(Ph₃P))⁺.

{{(N-Cyclohexyl-1-(4-methoxyphenyl)methaniminato-C6,N)(chloride)(triphenylphosphine)}palladium(II) (3b)} Prepared similarly to compound **3a**. Yellow solid, (25 mg, 59%), mp 176-178 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1580, $\nu(\text{Pd}-\text{Cl})$ 296 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 8.06 (d, ⁴*J*(PHi) = 10.0 Hz, 1H, HC=N), 7.86–7.70 (m, 6H, Ph₃P), 7.49-7.42 (m, 3H, Ph₃P), 7.39 (d, ³*J*(HH) = 7.6 Hz, 6H, Ph₃P), 7.20 (dd, ³*J*(H3H2) = 8.3 Hz, ⁴*J*(H3H5) = 2.3 Hz, 1H, H3), 6.43 (d, ³*J*(H2H3) = 8.3 Hz, 1H, H2), 6.00 (d, ⁴*J*(H5P) = 6.6 Hz, 1H, H5), 4.55-4.30 (m, 1H, N-CH-Cy), 2.97 (s, 3H, OMe), 2.26–0.88 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_{C} 167.6 (C=N), 161.5 (C4), 156.1 (C6), 152.4 (C1), 135.0 (C5), 128.2 (C3), 127.3 (C2), 69.8 (CH-N), 33-25 (CH₂). ³¹P NMR (162 MHz, CDCl₃) δ_{P} 42.74s. Anal. calcd for C₃₂H₃₃ClNOPd (620.47): C, 62.0; H, 5.4; N, 2.3. Found: C, 62.0; H, 5.3; N, 2.3%. ESI-MS: *m/z* = 619 ({(LH)Pd}{Cl}(Ph₃P))⁺.

{{(N-Cyclohexyl-1-(2-fluorophenyl)methaniminato-C6,N)(chloride)(bis(diphenylphosphino)methane-P,P)}palladium(II)-hexafluorophosphate, (4a)} To a stirred suspension of compound **2a** (50 mg, 0.048 mmol) in acetone (15 mL) at rt, was added dppm (36.9 mg, 0.096 mmol) and NH₄PF₆ in molar ratio 1:2. After 3 h a precipitate formed which was then filtered and dried in vacuum. Recrystallization gave the *title compound 4a* (84.3 mg, 71%) as a yellow solid, mp 167-169 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1588 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 8.53 (br s, 1H, HC=N), 7.81–7.33 (m, 20H, Ph₂P), 7.00-6.85 (m, 1H, H4), 6.76 (t, ³*J*(H3F) = 9.2 Hz, 1H, H3), 6.49 (dd, ⁴*J*(H5P) = 7.2 Hz, 1H, H5), 4.30 (br s, 2H, PCH₂P), 3.47–3.31 (m, 1H, N-CH-Cy), 2.20–0.60 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_{C} 167.1 (C=N), 163.7 (C2), 156.9 (C6), 152.8 (C1), 69.8 (CH-N), 35.9 (PCH₂P), 35-24 (CH₂). ³¹P NMR (162 MHz, CDCl₃) δ_{P} -4.96 (d, *J* = 67.0 Hz), -29.35 (d, *J* = 67.0 Hz), -152.28 (h, PF₆⁻). C₃₈H₃₇F₇NP₃Pd (840.04): C, 54.3; H, 4.4; N, 1.7. Found: C, 54.2; H, 4.3; N, 1.7%. ESI-MS: *m/z* = 839 ({(LH)Pd}{dppm})⁺.

{{(N-Cyclohexyl-1-(4-methoxyphenyl)methaniminato-C6,N)(chloride)(bis(diphenylphosphino)methane-P,P)}palladium(II)-hexafluorophosphate (4b)} Prepared similarly to compound **4a**. Yellow solid (95.5 mg, 82%), mp 153-155 °C (CH₂Cl₂/*n*-hexane). IR: $\nu(\text{C}=\text{N})$ 1574 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ_{H} 8.15 (d, ⁴*J*(PHi) = 7.6 Hz, 1H, HC=N), 7.80–7.32 (m, 20H, Ph₂P), 6.59 (dd, ³*J*(H3H2) = 8.3 Hz, ⁴*J*(H3H5) = 2.3 Hz, 1H, H3), 6.22 (dd, ⁴*J*(H5H3) = 2.3 Hz, ⁴*J*(H5P) = 8.1 Hz, ⁴*J*(H5P_{trans}) = 10.4 Hz, 1H, H5), 4.28 (dd, ²*J*(HP) = 11.3, 8.1 Hz, 2H, PCH₂P), 3.30 (s, 3H, OMe), 3.35-3.20 (m, 1H, N-CH-Cy), 2.20–0.60 (m, 10H, Cy). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ_{C} 169.0 (C=N), 162.3 (C4), 157.0 (C6), 153.3 (C1), 70.0 (CH-N), 35.1 (PCH₂P), 33-22 (CH₂). ³¹P NMR (162 MHz, CDCl₃) δ_{P} -4.12 (d, *J* = 61.0 Hz), -27.74 (d, *J* = 61.0 Hz), -141.29 (h, PF₆⁻). C₃₉H₄₀F₆NOP₃Pd (852.07): C, 55.0; H, 4.7; N, 1.6. Found: C, 54.9; H, 4.6; N, 1.6%. ESI-MS: *m/z* = 851 ({(LH)Pd}{dppm})⁺.

Catalytic activity. Treatment of 4-bromoacetophenone with phenylboronic acid in THF/water (2:1) at rt or at 80 °C for a maximum of 24 h in the presence of 2 mol% catalyst and base, K₂CO₃, gave the biphenyl coupled product 4-phenylacetophenone in >80% in the majority of cases (Table 1). The use of a solvent different from the one stated above gave poorer results.

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Supplementary Material

Bond lengths (Å) and angles (°) for compounds **3a** and **4b**. Secondary interaction lengths (Å) and angles (°) for compounds **3a** and **4b**. Crystal data and structure refinement for compound **3a**. Crystal data and structure refinement for compound **4b**. CCDC Identification numbers and NMR spectra.

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