A Platinum Open Access Journal for Organic Chemistry

Paper

Free to Authors and Readers | DOAJ Seal | *Arkivoc* **2022**, part ix, 186-198

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

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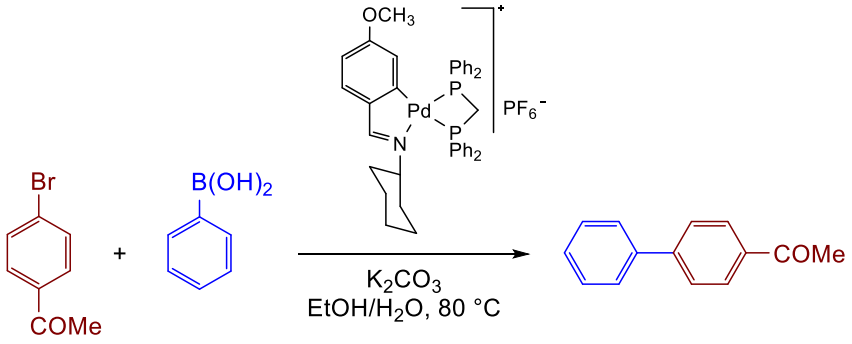
Received 09-08-2022 **Accepted Manuscript** 12-16-2022 **Published on line** 01-20-2023

Abstract

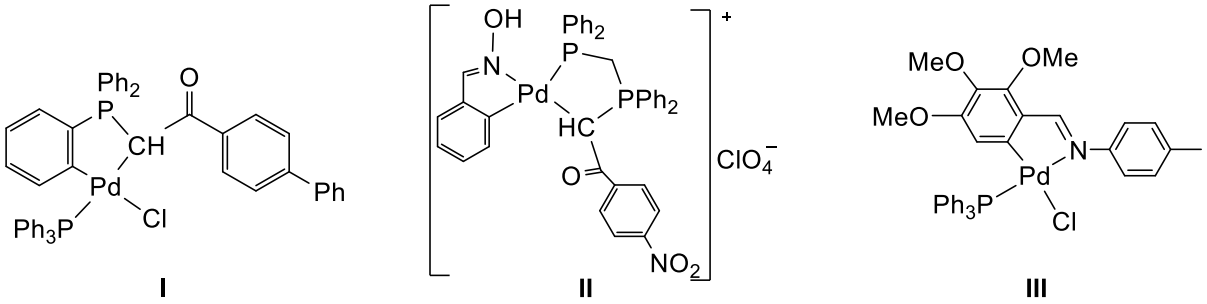
Palladacycles have been synthesized from $Pd(OAc)_2$ and Schiff base ligands via C-H activation, to render dinuclear acetate-bridged compounds. The latter are starting materials for the sequence of reactions leading to the ensuing complexes. Treatment of the μ-acetate dinuclear complexes with aqueous 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 $^{31}P\{^1H\}$ NMR spectroscopy. The crystal structures of two of them were determined by single-crystal X-ray diffraction. Additionally, the performance of the synthetized 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]



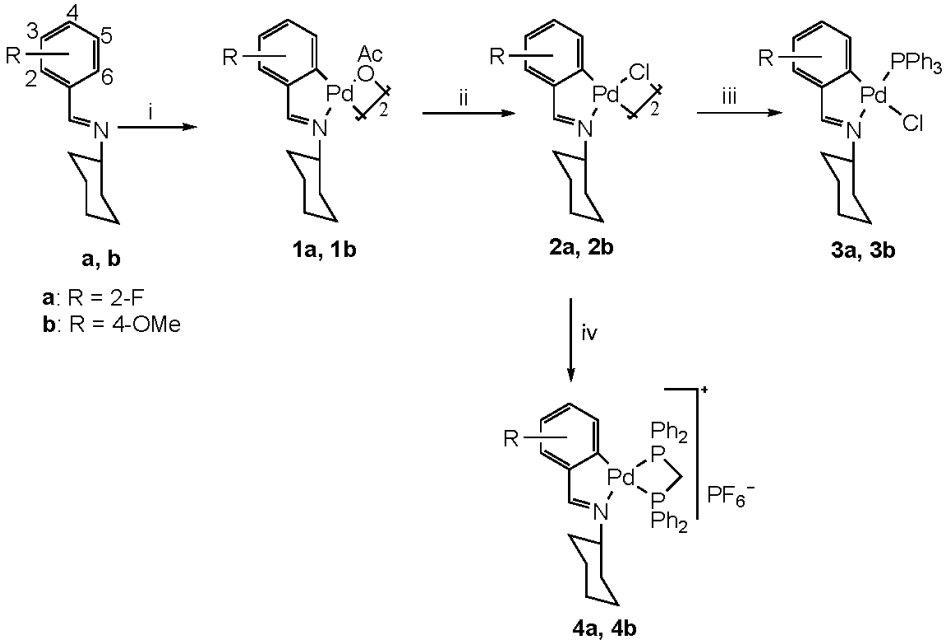
Scheme 1. Palladacycles active as catalysts in the Suzuki cross-coupling reaction.

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 ^{1}H-NMR, ^{31}P-{^{1}H} 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 *ν*(C=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 ν_{as}(COO) and ν_{s}(COO) vibrations in the IR spectra *ca*. 160 cm^{-1}.[25] In the ^{1}H 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 ^{1}H 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 *ν*(Pd–Cl) bands for each complex assigned to the *ν*(Pd-Cl)$_{trans\text{N}}$, (348, 320 cm^{-1})and *ν*(Pd-Cl)$_{trans\text{C}}$ (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 Pd_2Cl_2 bridging unit, and the ^{1}H NMR spectra confirmed the absence of the acetate ligand resonances. Single nuclear compounds were obtained by bridge-splitting reactions with monodentate (Ph_3P) and bidentate ($Ph_2PCH_2PPh_2$, dppm) phosphine ligands, **3a**, **3b** and **4a**, **4b**, respectively.



Scheme 2. i) $Pd(OAc)_2$, toluene, reflux; ii) NaCl (aq), acetone, 2 h; iii) Ph_3P, acetone, 3 h; iv) dppm, acetone, 3 h.

The signals for the *H*C=N protons were a broad singlet for compound **4a** and a doublet for the other compounds, indicating phosphorus nuclei coupling. The ^{31}P-{^{1}H} 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°].

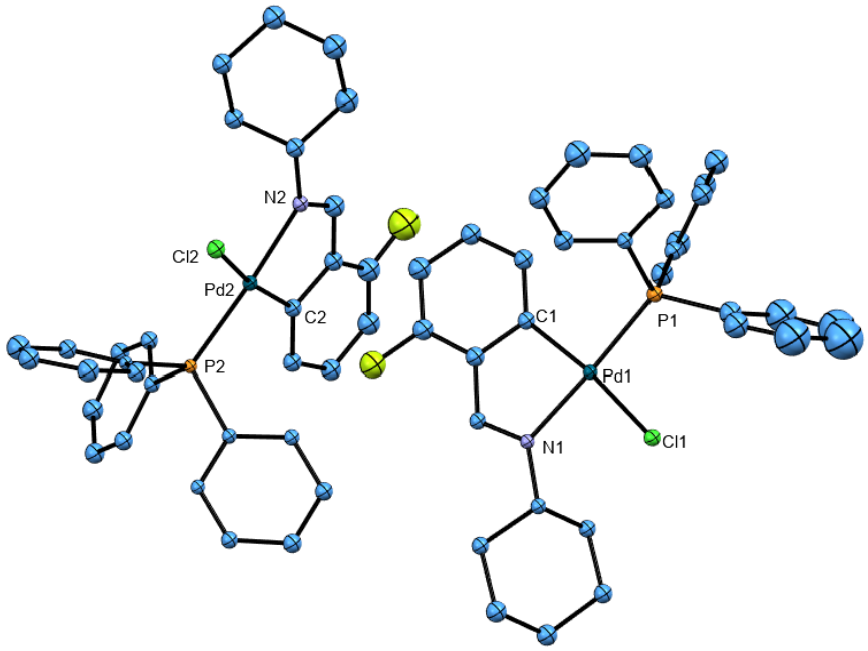


Figure 1. Thermal ellipsoid plot for **3a** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (˚): Pd(1)-C(1) 2.023(8), Pd(1)-N(1) 2.118(6), Pd(1)-Cl(1) 2.364(18), Pd(1)-P(1) 2.260(2), C(1)-Pd(1)-N(1) 81.9(3), N(1)-Pd(1)-Cl(1) 93.11(17), 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).

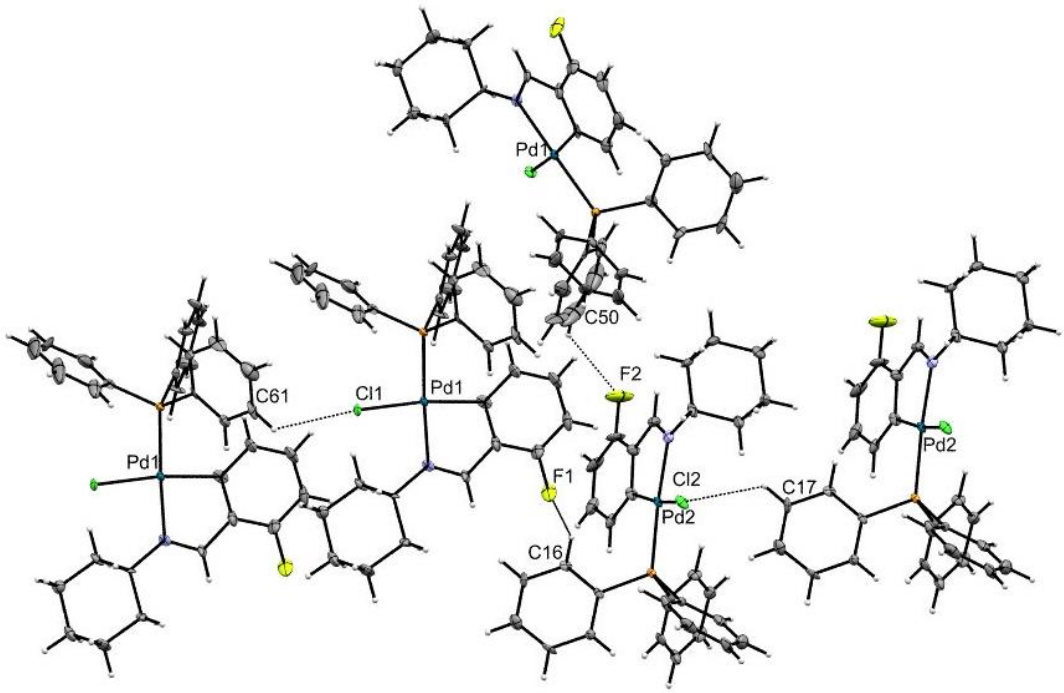


Figure 2. Intermolecular weak interaction in the crystal structure **3a**.

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°].

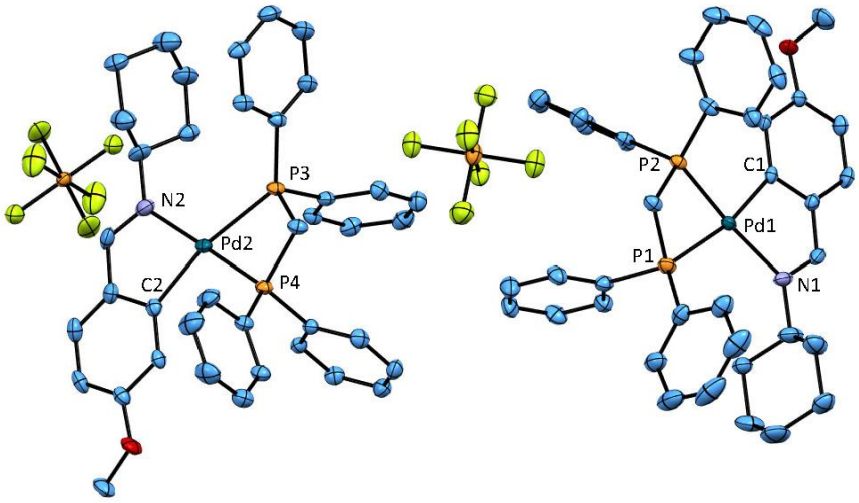


Figure 3. Thermal ellipsoid plot for **4b** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (˚): Pd(1)-C(1) 2.034(5), Pd(1)-N(1) 2.115(4), Pd(1)-P(1) 2.245(12), Pd(1)-P(2) 2.376(12), C(1)-Pd(1)-N(1) 81.25(3), N(1)-Pd(1)-P(1) 177.90(12), 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).

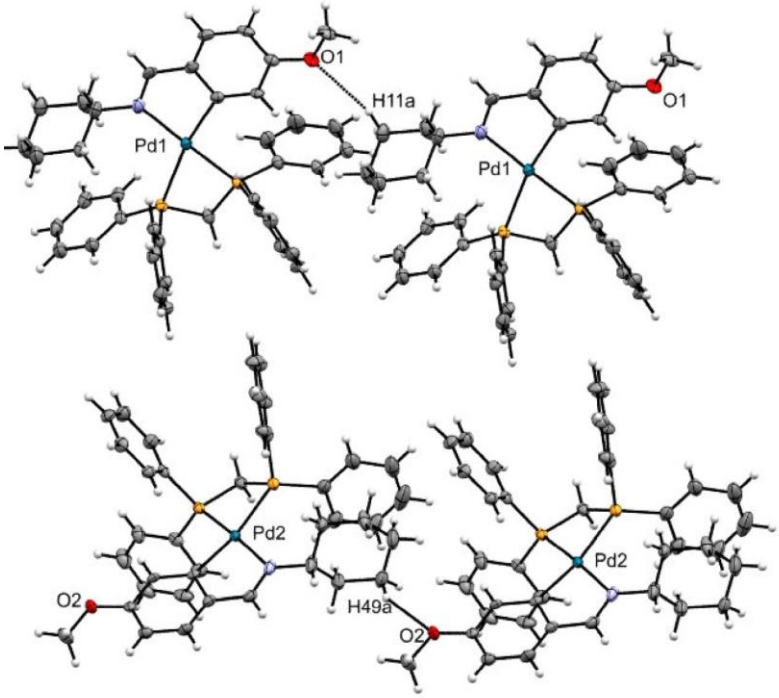
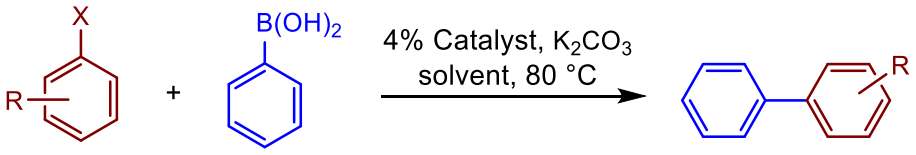


Figure 4. Intermolecular hydrogen weak interactions in the crystal structure of **4b**. solvent molecules and PF_6 ions have been omitted for clarity.

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 K_2CO_3 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



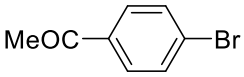
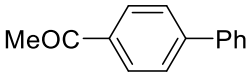
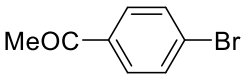
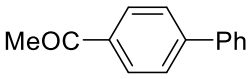
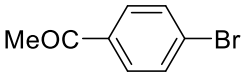
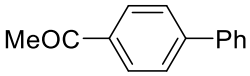
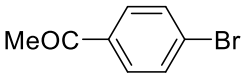
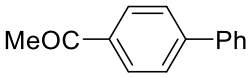
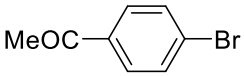
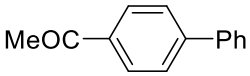
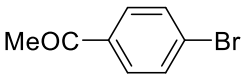
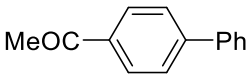
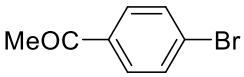
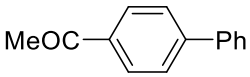
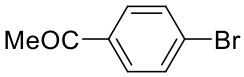
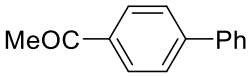
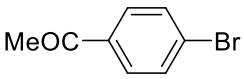
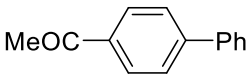
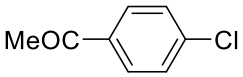
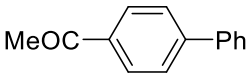
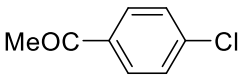
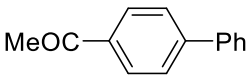
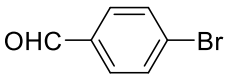
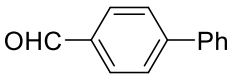
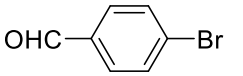
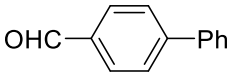
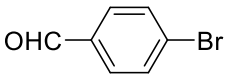
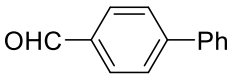
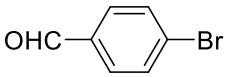
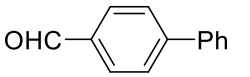
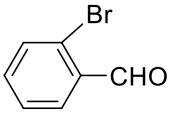
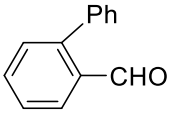
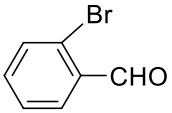
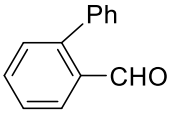
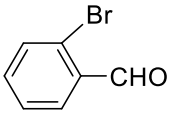
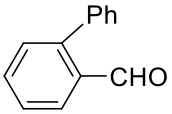
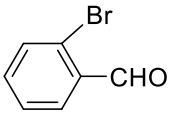
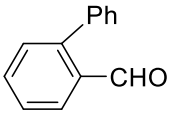
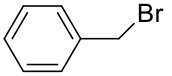
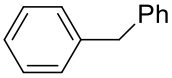
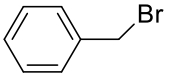
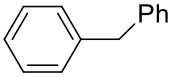
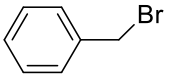
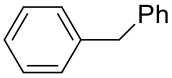
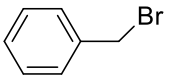
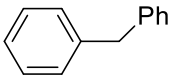
Entry	[cat.]	Aryl Halide	Product	Solvent[a,b]	Time (h)	Yield (%)
1	$Pd(OAc)_2$			THF/H_2O	24	64
2	**1a**			THF/H_2O	24	>99
3	**1b**			THF/H_2O	24	98
4	**2a**			THF/H_2O	24	95
5	**2b**			THF/H_2O	24	87
6	**3a**			THF/H_2O	24	>90
7	**3b**			THF/H_2O	24	>90
8	**4a**			EtOH/H_2O	17	>85
9	**4b**			EtOH/H_2O	17	>85
10	**1a**			THF/H_2O	24	100
11	**3b**			THF/H_2O	24	100
12	**1a**			THF/H_2O	24	25
13	**2b**			THF/H_2O	24	25
14	**3a**			THF/H_2O	24	>90
15	**4a**			THF/H_2O	24	>90

Table 1. Continued

Entry	[cat.]	Aryl Halide	Product	Solvent[a,b]	Time (h)	Yield (%)
16	**1a**			THF/H_2O	24	>90
17	**2b**			THF/H_2O	24	>90
18	**3a**			THF/H_2O	24	85
19	**4a**			THF/H_2O	24	88
20	**1a**			THF/H_2O	24	80
21	**2b**			THF/H_2O	24	88
22	**3a**			THF/H_2O	24	88
23	**4a**			THF/H_2O	24	83

Reaction conditions: Bromoarene (0.1 mmol), phenylboronic acid (1.2 equiv.), K_2CO_3 (2 equiv.), catalyst (4 mol %), 6 mL: [a] THF/H_2O (2:1), [b] EtOH/H_2O (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 Ph_3P 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 $Pd(Ph_3P)_4$ 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, $[Pd(C_{sp2},N\text{-imine})(\mu\text{-OAc})]_2$. 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, $[Pd(C_{sp2},N\text{-imine})(\mu\text{-Cl})]_2$, are easily obtained. Treatment of the latter in a bridge-splitting reaction with mono- or bidentate tertiary phosphines, Ph_3P and dppm, respectively, renders the single nuclear complexes $[PdCl(C_{sp2},N\text{-imine})(PR_3)]$ and $[Pd(C_{sp2},N\text{-imine})(Ph_2PCH_2PPh_2\text{-P,P})(PF_6)]$. 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. Solvents were purified by standard methods.[33] The reactions were carried out under dry nitrogen. Palladium(II) acetate, 4-methoxy-, 2-flourinebenzaldehydes 2-methylthioaniline, triphenylphosphine (Ph_3P) and bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, dppm) 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. ^{1}H NMR and spectra in solution were recorded in acetone-d_6 or $CDCl_3$ 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, $CDCl_3$ δ_H 7.26). Similarly, ^{13}C NMR {^{1}H} spectra were recorded at 100 MHz on a Bruker AMX 400 spectrometer. ^{31}P NMR spectra in solution were recorded in acetone-d_6 or $CDCl_3$ 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 H_3PO_4 (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-Flourobenzaldehyde (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}. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C{^{1}H} 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 (CH_2). Anal. calcd for $C_{13}H_{16}FN$ (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}. ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C{^{1}H} 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 (CH_2). Anal. calcd for $C_{14}H_{19}NO$ (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-C*6*,*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 (CH_2Cl_2/*n*-hexane). IR: *ν*(C=N) 1615, ν_{as}(COO) 1574, ν_s(COO) 1408 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ 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 (CH_2), 24.3 (CH_3). Anal. calcd for $C_{30}H_{38}F_2N_2O_4Pd_2$ (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 (CH_2Cl_2/*n*-hexane). IR: *ν*(C=N) 1609, ν_{as}(COO) 1570, ν_s(COO) 1414 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ 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 (CH_2), 25.0 (CH_3). Anal. calcd for $C_{32}H_{44}N_2O_6Pd_2$ (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 (CH_2Cl_2/*n*-hexane). IR: *ν*(C=N) 1615, (Pd–$Cl_{trans\text{-}N}$) 348, *ν*(Pd–$Cl_{trans\text{-}C}$) 287 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 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 $C_{27}H_{33}Cl_2F_2N_2Pd_2$ (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-C*6*,*N*)dipalladium(II) (2b). Prepared similarly to compound **2a**. Pale yellow solid, (220 mg, 46%), mp 236-238 °C (CH_2Cl_2/*n*-hexane). IR: *ν*(C=N) 1600, *ν*(Pd–$Cl_{trans\text{-}N}$) 320, *ν*(Pd–$Cl_{trans\text{-}C}$) 262 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 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 $C_{29}H_{39}Cl_2O_2N_2Pd_2$ (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-C*6*,*N*)(chloride)(triphenylphosphine)}palladium(II) (3a). Compound **2a** (25 mg, 0.036 mmol) and Ph_3P (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 (CH_2Cl_2/*n*-hexane). IR: *ν*(C=N) 1589, *ν*(Pd–Cl) 305 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ 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 (CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ_P 42.90s. Anal. calcd for $C_{31}H_{30}ClFNPPd$ (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 $(\{(LH)Pd\}(Cl)(Ph_3P))^+$.

{(*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 (CH_2Cl_2/*n*-hexane). IR: *v*(C=N) 1580, *v*(Pd–Cl) 296 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.06 (d, ^4J(PHi) = 10.0 Hz, 1H, HC=N), 7.86–7.70 (m, 6H, Ph_3P), 7.49-7.42 (m, 3H, Ph_3P), 7.39 (d, ^3J(HH) = 7.6 Hz, 6H, Ph_3P), 7.20 (dd, ^3J(H3H2) = 8.3 Hz, ^4J(H3H5) = 2.3 Hz, 1H, H3), 6.43 (d, ^3J(H2H3) = 8.3 Hz, 1H, H2), 6.00 (d, ^4J(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). $^{13}C\{^1H\}$ 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 (CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ_P 42.74s. Anal. calcd for $C_{32}H_{33}ClNOPPd$ (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)(Ph_3P))$^+$.

{(*N*-Cyclohexyl-1-(2-fluorophenyl)methaniminato-C*6*,*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 NH_4PF_6 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 (CH_2Cl_2/*n*-hexane). IR: *v*(C=N) 1588 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.53 (br s, 1H, HC=N), 7.81–7.33 (m, 20H, Ph_2P), 7.00-6.85 (m, 1H, H4), 6.76 (t, ^3J(H3F) = 9.2 Hz, 1H, H3), 6.49 (dd, ^4J(H5P) = 7.2 Hz, 1H, H5), 4.30 (br s, 2H, PCH_2P), 3.47–3.31 (m, 1H, N-CH-Cy), 2.20–0.60 (m, 10H, Cy). $^{13}C\{^1H\}$ 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 (PCH_2P), 35-24 (CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ_P -4.96 (d, *J* = 67.0 Hz), -29.35 (d, *J* = 67.0 Hz), -152.28 (h, PF_6^-). $C_{38}H_{37}F_7NP_3Pd$ (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-C*6*,*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 (CH_2Cl_2/*n*-hexane). IR: *v*(C=N) 1574 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.15 (d, ^4J(PHi) = 7.6 Hz, 1H, HC=N), 7.80–7.32 (m, 20H, Ph_2P), 6.59 (dd, ^3J(H3H2) = 8.3 Hz, ^4J(H3H5) = 2.3 Hz, 1H, H3), 6.22 (dd, ^4J(H5H3) = 2.3 Hz, ^4J(H5P) = 8.1 Hz, ^4J($H5P_{trans}$) = 10.4 Hz, 1H, H5), 4.28 (dd, ^2J(HP) = 11.3, 8.1 Hz, 2H, PCH_2P), 3.30 (s, 3H, OMe), 3.35-3.20 (m, 1H, N-CH-Cy), 2.20–0.60 (m, 10H, Cy). $^{13}C\{^1H\}$ 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 (PCH_2P), 33-22 (CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ_P -4.12 (d, *J* = 61.0 Hz), -27.74 (d, *J* = 61.0 Hz), -141.29 (h, PF_6^-). $C_{39}H_{40}F_6NOP_3Pd$ (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, K_2CO_3, 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.

Acknowledgements

We thank the Xunta de Galicia (Galicia, Spain) and the Competitive Reference Groups GRC2019/14 for their financial support.

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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