Inorganica Chimica Acta 363 (2010) 1262–1268

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Buchwald–Hartwig C–N cross coupling reactions catalyzed by a pseudo-pincer Pd(II) compound

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A R T I C L E I N F O

Article history:
Received 29 December 2009
Accepted 19 January 2010
Available online 25 January 2010

Dedicated to Jonathan R. Dilworth

Keywords:
C–N cross coupling reactions
Buchwald–Hartwig reaction
Palladium complexes
Palladacycles
Pincer compounds
Crystal structures
Catalysis

A B S T R A C T

The reaction of the imino compound $[C_6H_4\text{-}1\text{-}(OH)\text{-}3\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)]$ (**1**) with $[Pd(COD)Cl_2]$ affords in good yields the cyclometalated product $[PdCl(H_2NC_6H_2\text{-}2,4,6\text{-}Me_3)\{C_6H_3\text{-}2\text{-}(O\text{-}H)\text{-}6\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)\}]$ (**2**), both species being unequivocally identified by single crystal X-ray structure analysis. Careful analysis of both structures in the solid state reveals the presence of important hydrogen bond interactions, leading in the case of the Pd(II) derivative to the formation of a pseudo-pincer/non-covalent pincer compound $[PdCl(H_2NC_6H_2\text{-}2,4,6\text{-}Me_3)\{C_6H_3\text{-}2\text{-}(O\text{-}H)\text{-}6\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)\}]$ (**2**). The catalytic activity of this species was examined in Buchwald–Hartwig C–N cross coupling of morpholine with a series of *p*-substituted bromo-benzenes.

1. Introduction

Supramolecular chemistry [1] and catalysis [2] have had a renaissance in the last decade and this hand to hand progress was quickly adverted by chemist around the world, thus bringing together this two research areas for the creation of what is now called supramolecular catalysis [3]. Part of the aim of this crescent area of chemistry its been on the design and exploration of non-covalent interactions (e.g. hydrogen bond, etc.) in the creation of new catalysts, in principle more efficient for a given catalytic process, thus reducing either the loads of catalyst or mild the reaction conditions by reducing reaction times or temperatures. Taking advantage of these non-covalent interactions also may lead in principle to the easy creation and synthesis of a series of catalysts libraries for their exploration in different catalytic processes, by reducing tedious procedures of synthesis. This efforts have been well documented in different papers and a book dealing with this very much interesting area has been recently published [4]. On the other hand, the development of palladacycles [5] and particularly pincer compounds [6] have also been developed side by side of catalysis and both areas have advanced as a consequence of this symbiosis, thus pincer chemistry has gained a lot of interest in the last decade and several reviews [7] have been written regarding this chemistry, mainly on the design of new and every time more robust and catalytically active compounds. Thus, given our current interest in the chemistry of pincer compounds [8] and the study of supramolecular interactions [9] we would like to report in this paper the easy synthesis of a potentially interesting and versatile non-covalent pincer frame and the preliminary exploration of the catalytic activity of their palladium derivative on Buchwald–Hartwig C–N cross coupling reactions.

2. Experimental

2.1. Material and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The ^1H and ^{13}C NMR spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent ($CDCl_3$) as internal standard. Elemental analyzes were determined on a Perkin Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 keV xenon atoms. Mass

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doi:10.1016/j.ica.2010.01.023

measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. Melting points were determined in a MEL-TEMP capillary melting point apparatus and are reported without correction. GC–MS analyzes were performed on a Agilent 6890 N GC with a 30.0 m DB-1MS capillary column coupled to an Agilent 5973 Inert Mass Selective detector. The $PdCl_2$ was purchased from Pressure Chemical Co., and 3-hydroxy-benzaldehyde and 2,4,6-trimeyl-aniline were commercially obtained from Aldrich Chemical Co. All compounds were used as received without further purification. The starting material $[Pd(COD)Cl_2]$ was prepared according to published procedures [10].

2.2. Synthesis of $[C_6H_4\text{-}1\text{-}(OH)\text{-}3\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)]$ (**1**)

To 2,4,6-trimethyl-aniline (1.85 mL, 13.0 mmol) was added dropwise under stirring a solution of 3-hydroxy-benzaldehyde (1.58 g, 12.95 mmol) in CH_2Cl_2 (100 ml). The resulting solution was stirred for 10 min, after this time 30 g of activated molecular sieves were added. The reaction was then allowed to proceed under stirring for 24 h. After the prescribed reaction time, the mixture was filtered and washed with brine, dried (Na_2SO_4), filtered and evaporated under vacuum to afford ligand (**1**) (2.81 g, 11.78 mmol, 94%) as a microcrystalline white powder. m.p 106–107 °C. EI-MS: 239 (100, [*M*+]), 223 (20), 146 (70), 77 (10) *m/z* (%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.08 (s, 1H, CHN), 6.89–7.35 (m, 6H, Ar-H), 2.11 (s, 6H, CH_3), 2.26 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 164.04, 156.59, 148.08, 137.06, 133.62, 130.20, 128.97, 127.51, 121.61, 119.37, 114.55, 20.78, 18.29. IR (KBr): 3231 2916, 2721, 2585, 1632, 1593, 1451, 1374, 1298, 1276, 1207, 1139, 856, 786, 679 cm^{-1}. *Anal.* Calc. for $C_{16}H_{17}N_1O_1$ ($M_r = 239.31$): C, 80.30; H, 7.16. Found: C, 80.16; H, 7.17%.

2.3. Synthesis of $[PdCl(H_2NC_6H_2\text{-}2,4,6\text{-}Me_3)\{C_6H_3\text{-}2\text{-}(OH)\text{-}6\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)\}]$ (**2**)

A solution of $[Pd(COD)Cl_2]$ (143 mg, 0.5 mmol) in 10 mL of toluene was slowly added at room temperature to a stirred suspension of (**1**) (0.120 g, 0.5 mmol) and Na_2CO_3 (0.060 g, 0.5 mmol) in toluene (10 mL). The resulting reaction mixture was set to reflux for 24 h. After this time, the reaction was filtered and evaporated under vacuum to give complex (**2**) as a microcrystalline yellow solid (0.052 g, 62% with respect to the ligand). m.p 211 °C (decomp). Crystals suitable for X-ray analysis were obtained form a $CH_2Cl_2/^{i\text{-}}PrOH$ solvent system. ^1H NMR (300 MHz, $CDCl_3$): δ 6.65–7.05 (m, 7H, Ar-H), 7.73 (s, 1H, CHN), 2.17 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.25 (s, 3H, CH_3) 2.27 (s, 3H, CH_3) 3.39 (s, 2H, NH), $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 179.60, 161.89, 148.16, 143.34, 135.97, 132.42, 130.61, 128.30, 128.14, 126.08, 121.51, 119.04, 20.47, 20.03, 17.99, 17.67. IR (KBr): ν 3324, 3259, 2909, 1683, 1598, 1433, 1356, 1288, 1143, 1034, 851, 781,705, 682, 630, cm^{-1}. *Anal.* Calc. for $C_{25}H_{29}Cl_1N_2O_1Pd_1$ ($M_r = 515.38$): C, 58.26; H, 5.67. Found: C, 58.21; H, 5.65%.

2.4. Buchwald–Hartwig cross coupling reactions of aryl bromides; general procedure

A toluene solution (3 ml) of 1.2 mmol of halobenzene, 1.4 mmol of morpholine, and the prescribed amount of catalyst (0.1% mmol) was introduced into a Schlenk tube under nitrogen. The tube was charged with a magnetic stir bar and a slightly excess of base (^{t}BuOK, 1.70 mmol), sealed and then fully immersed in a 110 °C silicon oil bath. After the prescribed reaction time (12 h), the mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC–MS) by duplicate.

2.5. Mercury drop experiments

Following the above described procedures; additionally adding two drops of elemental Hg° to the reaction mixture. After the prescribed reaction times, a sample of the solution was analyzed by GC–MS: no significant difference in conversion between these experiments and those in the absence of mercury was observed, indicating that heterogeneous Pd(0) is not involved. These experiments were performed under the same condition for the experiments with bromobenzene.

2.6. Data collection and refinement for $[C_6H_4\text{-}1\text{-}(OH)\text{-}3\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)]$ (**1**) and $[PdCl(H_2NC_6H_2\text{-}2,4,6\text{-}Me_3)\{C_6H_3\text{-}2\text{-}(OH)\text{-}6\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)\}]$ (**2**)

Crystalline colorless prisms of $[C_6H_4\text{-}1\text{-}(OH)\text{-}3\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)]$ (**1**) and yellow prisms of $[PdCl(H_2NC_6H_2\text{-}2,4,6\text{-}Me_3)\{C_6H_3\text{-}2\text{-}(OH)\text{-}6\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)\}]$ (**2**) were grown by slow evaporation of CH_2Cl_2/*n*-heptane and $CH_2Cl_2/^iPrOH$ solvent systems respectively, and mounted in random orientation on glass fibers. In all cases, the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD-based three-circle X-ray diffractometer system using graphite mono-chromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package [11] using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic and triclinic unit cells to yield a total of 22 831 and 12 959 reflections for **1** and **2**, respectively, to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 5173 (**1**) and 4270 (**2**) were independent. Analysis of the data showed in all cases negligible decays during data collections. The structures were solved by Patterson method using SHELXS-97 [12] program. The remaining atoms were located via a few cycles of least-squares refinements and difference Fourier maps, using $P2_1/n$ and $P\bar{1}$ space groups for complexes **1** and **2**, respectively**,** with Z = 8 and 2 for compounds **1** and **2**, respectively. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups with $U_{iso}(H) = 1.2\,U_{eq}$ of the parent atom in all cases. For all complexes, the final cycle of refinement was carried out on all non-zero data using SHELXL-97 [13] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determinations are given in Table 1. The numbering of the atoms is shown in Figs. 1 and 3, respectively (ORTEP) [14]. Geometric calculations were done using PLATON [15].

3. Results and discussion

The reaction of 3-hydroxybenzaldehyde with 2,4,6-trimethyl aniline at room temperature under anhydrous conditions (Scheme 1) affords ligand $[C_6H_4\text{-}1\text{-}(OH)\text{-}3\text{-}(CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3)]$ (**1**) as a colorless microcrystalline product in high yields.

Analysis of this compound by infrared spectroscopy reveals a strong band at ν 1632 cm^{-1} due to the presence of the imino group, further, a broad signal about ν 2916 cm^{-1} exhibits the presence of the hydroxy group of the phenol. Analysis by ^1H NMR results more illustrative exhibiting signals between δ 2.11 and 2.26 ppm due to the methyl groups of the $CH{=}NC_6H_2\text{-}2,4,6\text{-}Me_3$ fragment. Additionally signals between δ 6.89–7.35 ppm correspond to the protons on

Table 1
Crystal data and structure parameters for [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**) and [PdCl($H_2NC_6H_2$-2,4,6-Me_3){C_6H_3-2-(OH)-6-(CH=NC_6H_2-2,4,6-Me_3)}] (**2**).

Identification code	(**1**)	(**2**)
Empirical formula	$C_{16}H_{17}N_1O_1$	$C_{25}H_{29}Cl_1N_2O_1Pd_1$
Formula weight	239.31	515.35
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.0503(14)	7.9411(9)
b (Å)	10.0949(13)	11.3634(12)
c (Å)	25.447(3)	13.7500(15)
α (°)	90	75.157(2)
β (°)	92.911(2)	82.027(2)
γ (°)	90	79.409(2)
V ($Å^3$)	2835.0(6)	1173.4(2)
Z	8	2
D_{calc} (Mg/m^3)	1.121	1.459
Absorption coefficient (mm^{-1})	0.070	0.923
F(0 0 0)	1024	528
Crystal size (mm)	0.38 × 0.20 × 0.20	0.274 × 0.186 × 0.098
θ (°)	1.97–25.34	1.88–25.35
Index ranges	$-13 \leqslant h \leqslant 13$, $-12 \leqslant k \leqslant 12$, $-30 \leqslant l \leqslant 30$	$-9 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 16$
Reflections collected	22 831	12 959
Independent reflections (R_{int})	5173 (0.0543)	4270 (0.0291)
Absorption correction	none	semi-empirical from equivalents
Maximum, minimum transmission	N/A	0.9187, 0.7941
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5173/0/337	4270/2/286
Goodness-of-fit (GOF) on F^2	0.882	1.039
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0374$, $wR_2 = 0.0843$	$R_1 = 0.0326$, $wR_2 = 0.0743$
R indices (all data)	$R_1 = 0.0702$, $wR_2 = 0.0925$	$R_1 = 0.0383$, $wR_2 = 0.0768$
Largest difference peak and hole ($eÅ^{-3}$)	0.117 and −0.123	0.525 and −0.220

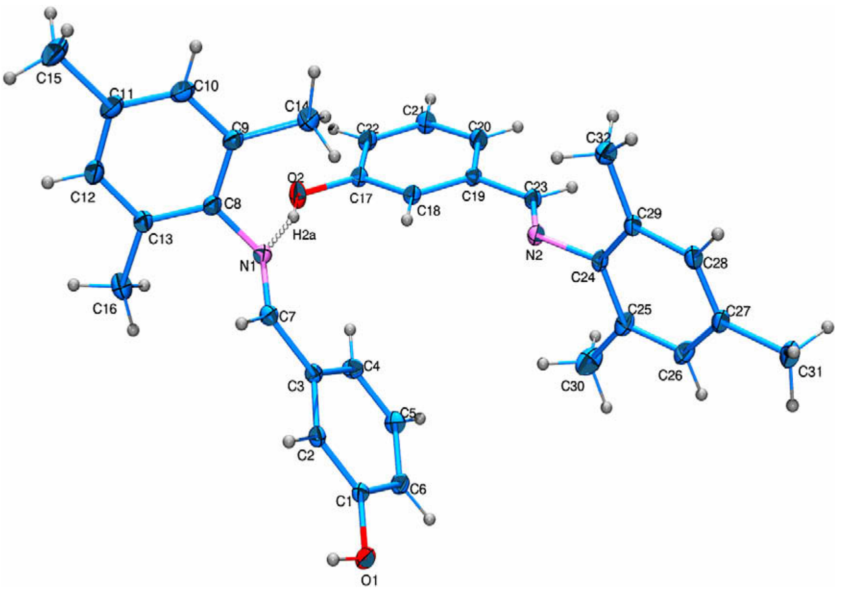


Fig. 1. An ORTEP representation of the structure of the ligand [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**) at 50% of probability showing the atom labeling scheme. Selected Bond lengths (Å): O(1)–C(1) 1.3576(17), O(1)–H(1) 0.913(16), N(1)–C(7) 1.2688(17), N(1)–C(8) 1.4358(18), O(2)–C(17) 1.3565(17), O(2)–H(2A) 0.898(19), N(2)–C(23) 1.2640(17), N(2)–C(24) 1.4384(18). Selected bond angles (°): C(1)–O(1)–H(1) 108.8(10), C(7)–N(1)–C(8) 116.54(13), C(17)–O(2)–H(2A) 113.1(11), C(23)–N(2)–C(24) 120.39(13).

the aromatic rings of the molecule. However, most significantly results the presence of a singlet at δ 8.08 ppm, this signal being indicative of the presence of the iminic proton C*H*=NC_6H_2-2,4,6-Me_3. Relevant from the analysis by $^{13}C\{^1H\}$ NMR is the signal at δ 164.04 ppm due to the iminic carbon *C*H=NC_6H_2-2,4,6-Me_3, other signals due to the aromatic carbons are observed at δ 156.59, 148.08, 137.06, 133.62, 130.20, 128.97, 127.51, 121.61, 119.37, 114.55 ppm, while signals at δ 20.78 and 18.29 ppm are consistent with the presence of the methyl substituents. EI-Mass spectroscopy spectrum shows a peak at $[M^+] = 239$ *m*/*z* (100%)

corresponding to the molecular ion with the proper isotopic distribution. Results from elemental analysis are also coherent with the proposed formulation and structure.

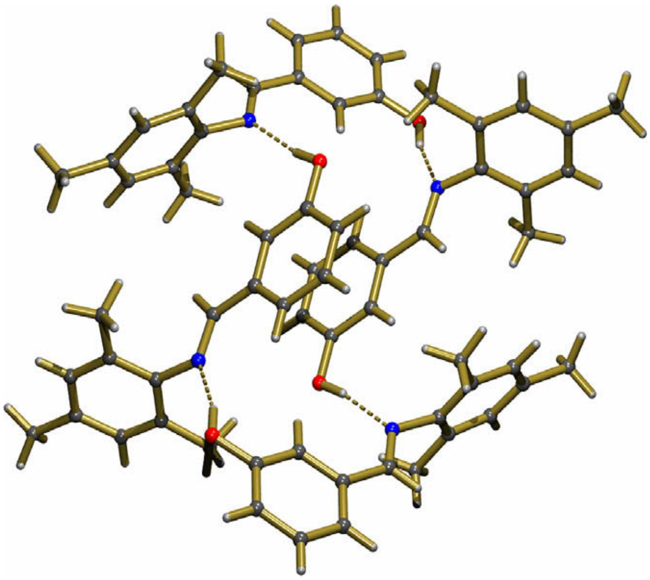


Fig. 2. A PLATON representation of the structure of ligand [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**) showing the hydrogen bond O–H···N and π–π interactions in the unit cell.

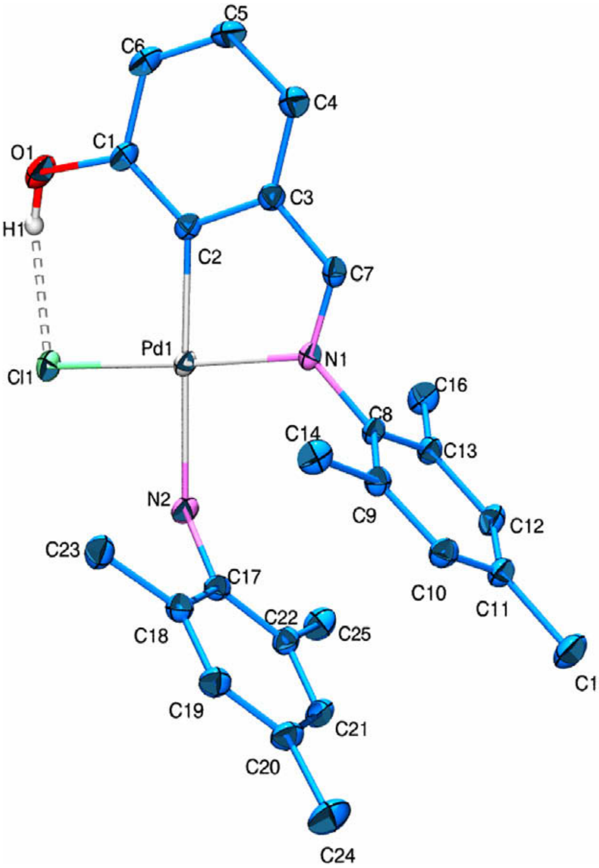
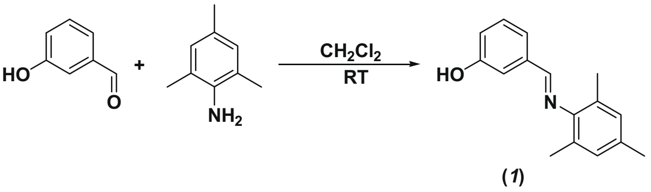


Fig. 3. An ORTEP representation of the structure of [PdCl($H_2NC_6H_2$-2,4,6-Me_3){C_6H_3-2-(OH)-6-(CH=NC_6H_2-2,4,6-Me_3)}] (**2**) at 50% of probability showing the atom labeling scheme. Selected bond lengths (Å): Pd(1)–C(2) 2.007(3), Pd(1)–N(1) 2.049(2), Pd(1)–N(2) 2.215(3), Pd(1)–Cl(1) 2.3293(8). Selected bond angles (°):C(2)–Pd(1)–N(1) 80.69(10), C(2)–Pd(1)–N(2) 177.36(10), N(1)–Pd(1)–N(2) 99.08(9), C(2)–Pd(1)–Cl(1) 97.45(8), N(1)–Pd(1)–Cl(1) 177.64(6), N(2)–Pd(1)–Cl(1) 82.71(7).



Scheme 1. Synthesis of the ligand [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**).

Attempts to crystallize compound [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**) from a CH_2Cl_2/*n*-heptane solvent system yielded crystals suitable for single crystal X-ray diffraction analysis. This analysis confirmed unequivocally the proposed structure of ligand (**1**) (Fig. 1).

Fig. 1 exhibits the structure of ligand (**1**) as determined by spectroscopic techniques. A close examination shows the unit cell to be supported mainly by hydrogen bonds O–H···N (Table 2) and aromatic π–π interactions (3.792 Å) (Fig. 2).

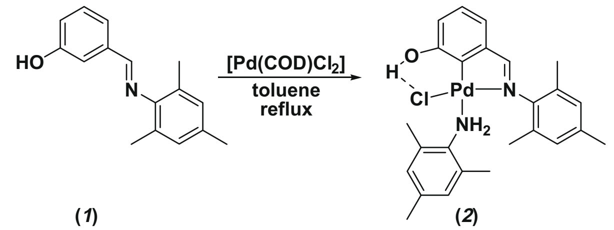
Initial interest in the synthesis of the above mentioned compound raised from the idea of synthesizing asymmetric pincer compounds, however we quickly realize that the use of the imine compound (**1**) may well lead to the attaining of a new palladacycle. Thus, with the ligand [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**) on hand we decided to explore its reactivity with the palladium starting material [Pd(COD)Cl_2]. Thus the stoichiometric reaction (Scheme 2) under reflux conditions in toluene afforded a yellow microcrystalline product of [PdCl($H_2NC_6H_2$-2,4,6-Me_3){C_6H_3-2-(OH)-6-(CH=NC_6H_2-2,4,6-Me_3)}] (**2**) in good yields. The resulting species is both air and moisture stable and can be handled on air without any apparent decomposition.

Initial analysis of this product by infrared spectroscopy exhibits absorptions at *ν* 3324 (w), 3259 (s), 2909 (w, br) cm^{-1} indicative of the presence of both the amine ligand $H_2NC_6H_2$-2,4,6-Me_3 and the hydroxy fragment of complex (**2**). An additional band at *ν* 1683 cm^{-1} reveals the presence of the imine moiety, the shift of 51 cm^{-1} (*vide supra*) clearly illustrate the effect of the coordination to the metal center. Analysis by ^{1}H NMR provides further information that supports the proposed structure. Thus, signals between δ 2.17 and 2.19 ppm are due to the methyl groups in the 2 and 6 positions of both the amine and imine aromatic fragments in the molecule, analogously signals between δ 2.25 and 2.27 ppm are

Table 2
Hydrogen bonds for [C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)] (**1**) [Å and °].

D–H···A	*d*(D–H)	~(H···A)	*d*(D···A)	<(D–H···A)
O(1)–H(1)···N(2)#1	0.913(16)	1.911(17)	2.8091(17)	167.2(16)
O(2)–H(2A)···N(1)	0.898(19)	1.868(19)	2.7454(17)	165.3(17)

Symmetry transformations used to generate equivalent atoms: #1 −x + 1,−y + 1,−z + 1.



Scheme 2. Synthesis of complex [PdCl($H_2NC_6H_2$-2,4,6-Me_3){C_6H_3-2-(OH)-6-(CH=NC_6H_2-2,4,6-Me_3)}] (**2**).

due to the methyls in the position 4 of the same fragments. Additionally, a broad signal at δ 3.34 ppm can be assigned to the protons on the amine ligand. Moreover, on the usual area for aromatic protons a set of signals can be observed between δ 6.65 and 7.05 ppm due to the protons on the aromatic rings of the molecule. Finally, as evidence for the presence of the imine group a sharp singlet is observed at δ 7.74 ppm due to the iminic proton (HC=N–R), once again the shift of this signal to higher field clearly evidences the coordination to the metal center.

Analysis by ^{13}C{^{1}H} NMR also shows some interesting features, exhibiting signals at δ 179.77, 162.71 and 147.27 ppm due to the iminic carbon (HC=N–R), the phenolic carbon (HO–C_{Ar}) and the carbon directly bonded to the C_{Ar}–NH$_2$ group, respectively. Additionally a set of signals at δ 143.34, 135.97, 132.42, 130.61, 128.30, 128.14, 126.08, 121.51, 119.04 ppm can be assigned to the carbon atoms on the aromatic rings. Finally, signals between δ 20.47 and 17.67 ppm are due to the methyl groups in the aromatic rings of both the amine and imine fragments.

Although the molecular ion is not observed, further analysis by FAB^{+}-MS shows a peak at 497 (12%) *m*/*z* due to the fragment [M^{+}−OH], other important fragments are observed at [M^{+}−Cl] = 479 (12%) and [M^{+}−Cl–(H$_2$NC$_6$H$_2$-2,4,6-Me$_3$)] = 344 (22%) *m*/*z*. These results together with those of the elemental analyzes are also coherent with the proposed formulation.

Recrystallization of [PdCl(H$_2$NC$_6$H$_2$-2,4,6-Me$_3$){C$_6$H$_3$-2-(OH)-6-(CH=NC$_6$H$_2$-2,4,6-Me$_3$)}] (**2**) from a CH$_2$Cl$_2$/^{i}PrOH solvent system at room temperature, afforded crystals suitable for single crystal X-ray diffraction analysis, revealing unequivocally the identity of complex (**2**) (Fig. 3).

The structure shows the palladium center into a slightly distorted square planar environment, two of the coordination sites being occupied by the five membered C–N palladacycle and completing the coordination sphere the chloride and amine (H$_2$NC$_6$H$_2$-2,4,6-Me$_3$) ligands (Fig. 3). Noteworthy is the fact that a strong hydrogen bond O1–H1···Cl1 (2.14 Å) gives place to a six member pseudo-palladacycle (Table 3), thus conforming a non-covalent pincer compound for (**2**). Other important hydrogen bonding interactions of the type N–H···Cl are also present in the unit cell for this complex, similar interactions have been reported previously by our group [16] (Fig. 4).

The advancement on the development of the cross coupling reactions has been accompanied by the development of the palladium chemistry, this being particularly true in the case of palladacycles and more specifically in the case of pincer compounds. With this in mind and the fact that complex [PdCl(H$_2$NC$_6$H$_2$-2,4,6-Me$_3$){C$_6$H$_3$-2-(OH)-6-(CH=NC$_6$H$_2$-2,4,6-Me$_3$)}] (**2**) showed a good thermal stability (m.p. 211 °C), similar to other genuine pincer compounds and base on the experience our research group has in the use of this sort of complexes in transition metal catalyzed reactions [6–8], we decided to explore the reactivity of the pseudo-pincer compound (**2**) in still one of the most challenging cross coupling processes, the C–N Buchwald–Hartwig reaction [17] (Scheme 3).

Thus, the *p*-bromobenzenes-morpholine system was chosen as a model reaction using potassium *tert*-butoxyde as base. The results attained are included in Table 4.

Table 3
Hydrogen bonds for [PdCl(H$_2$NC$_6$H$_2$-2,4,6-Me$_3$){C$_6$H$_3$-2-(OH)-6-(CH=NC$_6$H$_2$-2,4,6-Me$_3$)}] (**2**) [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(D–H···A)
O(1)–H(1)···Cl(1)	0.820(5)	2.14(5)	2.942(3)	165.0(5)
N(2)–H(2B)···Cl(1)	0.856(19)	2.755(18)	3.506(3)	147.0(2)

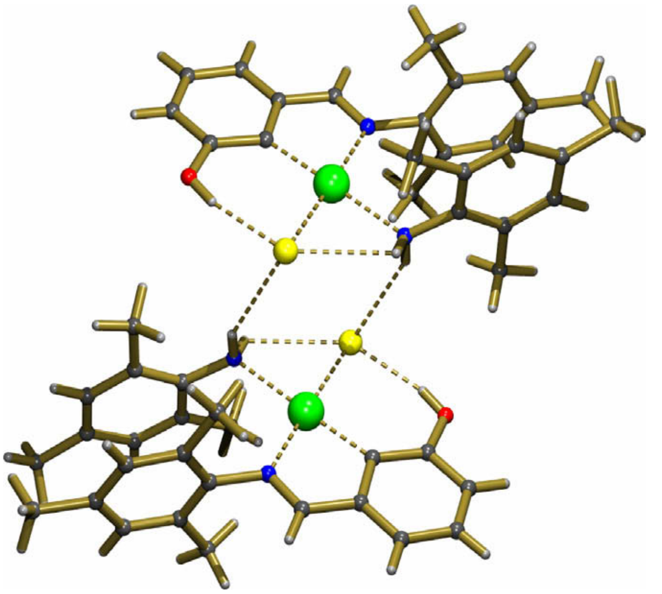
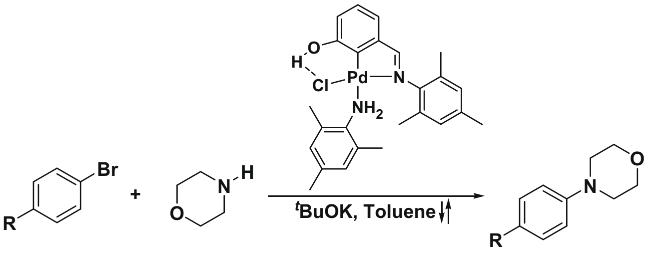


Fig. 4. A PLATON representation of the structure of complex [PdCl(H$_2$NC$_6$H$_2$-2,4,6-Me$_3$){C$_6$H$_3$-2-(OH)-6-(CH=NC$_6$H$_2$-2,4,6-Me$_3$)}] (**2**) showing hydrogen bonds O–H···Cl and N–H···Cl in the unit cell.

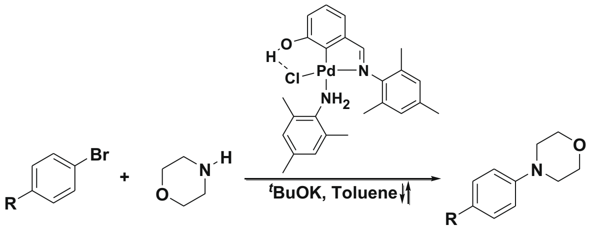


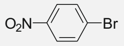
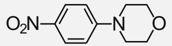
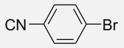
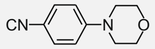
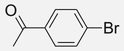
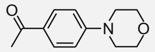
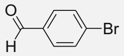
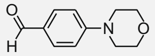
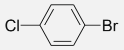
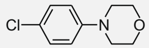
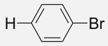
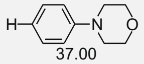
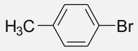
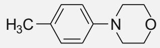
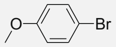
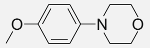
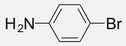
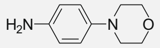
Scheme 3. Hartwig–Buchwald C–N cross coupling reactions mediated by [PdCl(H$_2$NC$_6$H$_2$-2,4,6-Me$_3$){C$_6$H$_3$-2-(OH)-6-(CH=NC$_6$H$_2$-2,4,6-Me$_3$)}] (**2**).

From this table a clear trend can be observed, which is dependant upon the kind of substituent in the bromobenzene, thus the more electro-withdrawing is the group the higher the conversion to the amine product. This trend can be better observed when the percentage of conversion is plotted against the Hammett parameter [18] (Graphic 1) where a near linear behavior can be clearly noted.

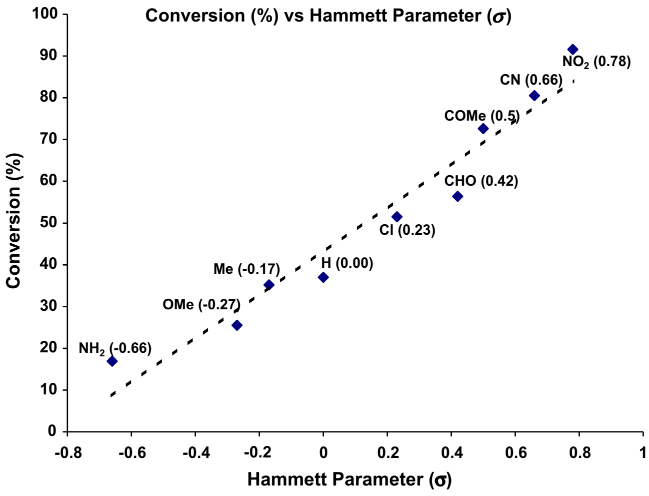
As with so many other palladacycle examples, it is possible that the reaction may proceed trough the formation of soluble palladium nanoparticles [19]. Hence, in order to rule out this possibility a Mercury drop experiment [20] (see Section 2) was performed noticing no appreciable difference in the performance of the catalyst with or without the presence of elemental mercury. There has been a considerable debate in the literature about the oxidation states of the species involved in the catalytic cycle with Pd(IV)/Pd(II) and Pd(II)/Pd(0) both being proposed at various times [21]. However, in this case we favor the Pd(IV)/Pd(II), although in this case the presence of the strong hydrogen bond and the imine group may led to the behavior of the ligand as a hemilabile pincer compound in solution [22] (a possibility that can not be ruled out). However, it is more plausible to think that the amine ligand will be lost in the process generating a coordinative unsaturated species which in turn might led to the coordination of the substrates and start the catalytic cycle. Another possibility that can not be ruled out is the potential enhancement in reactivity due to potential interactions in solution due to the presence of the hydroxy group, this enhancement in reac-

Table 4
Buchwald–Hartwig C–N cross couplings using [PdCl($H_2NC_6H_2$-2,4,6-Me_3){C_6H_3-2-(OH)-6-(CH=NC_6H_2-2,4,6-Me_3)}] (**2**) as catalyst precursor.



Entry	*p*-Bromobenzene	% Conversion[a]
1		 91.6
2		 80.50
3		 72.60
4		 56.40
5		 51.50
6		 37.00
7		 35.20
8		 25.50
9		 16.90

[a] Yields obtained by GC are based on bromobenzenes and are the average of two runs.



Graphic 1. Conversion (%) vs. Hammett parameter (σ).

tivity has been well documented and it is considered as one of the corner stones of supramolecular catalysis [23].

In summary, we have successfully synthesized a potentially important example of a Pd(II) pseudo-pincer/non-covalent pincer compound and tested its catalytic performance in C–N Buchwald–Hartwig cross coupling reactions exhibiting moderated to good activities depending of the electron-withdrawing capabilities of the *para*-substituent in the bromobenzene. The present system is interesting given the number of primary amines commercially available, thus a tuning of both sterics and electronics can be envisioned in order to improve the catalytic performance of the proposed complexes thus allowing the creation of a library of catalyst. Another attractive characteristic of the present system is the easy synthesis form cheap commercially available starting materials, thus turning this system attractive for its potential application in organic synthesis. Efforts aimed to achieve these goals are currently under development in our laboratories.

Acknowledgments

We would like to thank Chem. Eng. Luis Velasco Ibarra, Dr. Francisco Javier Pérez Flores for their invaluable help in the running of the FAB$^+$-MS. The financial support of this research by CONACYT (F58692) and DGAPA-UNAM (IN227008) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 759800 and 759801 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.01.023.

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