



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

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ABSTRACT

The reaction of the imino compound $[C_6H_4-1-(OH)-3-(CH=NC_6H_2-2,4,6-Me_3)]$ (**1**) with $[Pd(COD)Cl_2]$ affords in good yields the cyclometalated product $[PdCl(H_2NC_6H_2-2,4,6-Me_3)(C_6H_3-2-(O-H)-6-(CH=NC_6H_2-2,4,6-Me_3))]$ (**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 $[PdCl(H_2NC_6H_2-2,4,6-Me_3)(C_6H_3-2-(O-H)-6-(CH=NC_6H_2-2,4,6-Me_3))]$ (**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.

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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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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 PdCl₂ was purchased from Pressure Chemical Co., and 3-hydroxy-benzaldehyde and 2,4,6-trimethyl-aniline were commercially obtained from Aldrich Chemical Co. All compounds were used as received without further purification. The starting material [Pd(COD)Cl₂] was prepared according to published procedures [10].

2.2. Synthesis of [C₆H₄-1-(OH)-3-(CH=NC₆H₂-2,4,6-Me₃)] (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 CH₂Cl₂ (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 (Na₂SO₄), 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, CDCl₃): δ 8.08 (s, 1H, CHN), 6.89–7.35 (m, 6H, Ar-H), 2.11 (s, 6H, CH₃), 2.26 (s, 3H, CH₃). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): 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 C₁₆H₁₇N₁O₁ (M_r = 239.31): C, 80.30; H, 7.16. Found: C, 80.16; H, 7.17%.

2.3. Synthesis of [PdCl(H₂NC₆H₂-2,4,6-Me₃){C₆H₃-2-(OH)-6-(CH=NC₆H₂-2,4,6-Me₃)] (2)

A solution of [Pd(COD)Cl₂] (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 Na₂CO₃ (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 from a CH₂Cl₂/PrOH solvent system. ¹H NMR (300 MHz, CDCl₃): δ 6.65–7.05 (m, 7H, Ar-H), 7.73 (s, 1H, CHN), 2.17 (s, 6H, CH₃), 2.19 (s, 6H, CH₃), 2.25 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 3.39 (s, 2H, NH). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): 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 C₂₅H₂₉Cl₁N₂O₁Pd₁ (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 (^tBuOK, 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 Hg⁰ 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 [C₆H₄-1-(OH)-3-(CH=NC₆H₂-2,4,6-Me₃)] (1) and [PdCl(H₂NC₆H₂-2,4,6-Me₃){C₆H₃-2-(OH)-6-(CH=NC₆H₂-2,4,6-Me₃)] (2)

Crystalline colorless prisms of [C₆H₄-1-(OH)-3-(CH=NC₆H₂-2,4,6-Me₃)] (1) and yellow prisms of [PdCl(H₂NC₆H₂-2,4,6-Me₃){C₆H₃-2-(OH)-6-(CH=NC₆H₂-2,4,6-Me₃)] (2) were grown by slow evaporation of CH₂Cl₂/*n*-heptane and CH₂Cl₂/PrOH 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 (λ = 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 P2₁/n and P1̄ 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 [C₆H₄-1-(OH)-3-(CH=NC₆H₂-2,4,6-Me₃)] (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=NC₆H₂-2,4,6-Me₃ fragment. Additionally signals between δ 6.89–7.35 ppm correspond to the protons on

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