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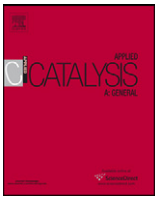

Oxadiazoline and ketoimine palladium(II) complexes supported on a chitosan membrane and their catalytic activity for the microwave-assisted Suzuki–Miyaura cross-coupling in water

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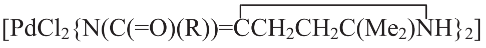
ABSTRACT

The fused bicyclic Δ^4-1,2,4-oxadiazoline trans-( $[PdCl_2\{N{=}C(R)ONC(H)CH_2CH_2CMe_2\}_2]$) palladium(II) complex 1 ($R = p\text{-}ClC_6H_4$), in refluxing chloroform, undergoes N–O bond cleavage of the oxadiazoline ring to furnish the new ketoimine palladium(II) complex trans-( $[PdCl_2\{N(C({=}O)(R)){=}CCH_2CH_2C(Me_2)NH\}_2]$) 2 bearing the 4-chloro-N-(5,5-dimethylpyrrolidin-2-ylidene)benzamide ligands. Complexes 1 (R = Me) and 2 ($R = p\text{-}ClC_6H_4$) were immobilized on a chitosan membrane and the systems acted as supported-catalysts (Pd-chit 1 and Pd-chit 2, respectively) for the model microwave-assisted Suzuki–Miyaura cross-coupling reactions in water using *p*-bromoanisole and phenylboronic acid to give *p*-methoxybiphenyl in excellent yield. The effects of catalyst loading, temperature, time, the phase-transfer agent tetrabutylammonium bromide (TBAB) and base were investigated, and the supported catalyst was recovered and reused up to seven times, with a gradual loss of catalytic activity.

1. Introduction

The Suzuki–Miyaura cross-coupling reaction, leading to palladium-catalyzed carbon–carbon bond formation from organoborates and organo-halides, organo-triflates or organo-tosylates, has become an efficient strategy for the preparation of biphenyls [1–5]. In this reaction, homogenous catalytic systems have been proven to be efficient and palladium complexes are usually used as the catalysts. Very recently, we reported that palladium(II) complexes containing (pyrrolidin-2-ylidene)-phthalamide [6], dihydropyrrolyl-iminoisoindolinone [6], Δ^4-1,2,4-oxadiazoline [7] and (pyrrolidin-2-ylidene)picolinamide [8] ligands show remarkably high catalytic activities towards the Suzuki–Miyaura cross-coupling reaction under thermal and microwave (M.W.) conditions. M.W. is an alternative way to the traditional heating with the possible advantages of reducing the reaction time, increasing the yield, the selectivity and purity of the products [1,7–11].

However, the homogenous catalytic systems have usually problems associated with the separation, recovery and the use of high temperatures. These problems can be overcome by the use of heterogenized catalysts, made up of supported palladium complexes. Different supports have been used, such as polymers, carbon, clays, zeolites molecular sieves and silica [12–28]. However, increasing attention has recently been paid to the use of biomaterials for the immobilization of metal complexes [29–35].

Chitosan is the *N*-deacetylated derivative of chitin and has good properties of natural polymers, such as non-toxicity, biodegradability and biocompatibility, which make it an environmentally friendly material [29,30]. Hydrophilicity is a very important characteristic of chitosan and it has also been used widely as an adsorbent for transition metal ions like Pd, Cu, Ni, Zn, Pb, because the amino ($-NH_2$) and hydroxy (–OH) groups on chitosan chains can serve as coordination and further functionalization sites [29–32,36–43]. In this context, several groups have demonstrated the catalytic activity of chitosan-supported catalysts in hydrogenation [44], polymerization [45], oxidation [46], cyclopropanation of alkenes [47], etc. Hardy et al. [48] modified chitosan by the introduction of a palladium iminopyridyl complex and the catalyst was used for the Suzuki–Miyaura and Heck reactions; Cui et al. [49] used a chitosan–palladium complex as catalyst for the Heck reaction. In addition, Lee et al. [50] reported the Suzuki–Miyaura reaction by using a chitosan-supported ligand-free palladium (0) catalyst in water. However, there are only a few reports [50,51] on the use of chitosan-supported catalysts for the microwave-assisted Suzuki–Miyaura cross-coupling reaction in aqueous medium. Fur-

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thermore, incorporation of palladium complexes on catalytic membrane reactors is an emerging novel technology that can provide an environmentally friendly system [52,53].

Hence, the main general aims of the current work are: (i) to immobilize the oxadiazoline and derived ketoimine complexes on the chitosan membrane to form heterogenized palladium(II) species (Pd membrane systems remain very little explored); (ii) to investigate the catalytic activity of the chitosan-supported catalysts for the Suzuki–Miyaura reaction; (iii) to use water as solvent (a non-flammable, safe and cheap "green" solvent with a high separation potential since the organic products can be readily separated from the aqueous layer); (iv) to study the effects of the main factors on the cross-couplings; (v) to investigate the possibility of recovering and reusing the catalyst; (vi) to apply focused M.W. irradiation on attempting to reduce the reaction time and to increase the yield in comparison with traditional heating methods [1,7–11]. In this context, we now report the catalytic activity of oxadiazoline and ketoimine palladium(II) complexes supported on a chitosan membrane for the microwave-assisted Suzuki–Miyaura reaction in pure water.

2. Experimental

Solvents and reagents were obtained from commercial sources (Aldrich) and used as received. The starting oxadiazoline-Pd^{II} complexes *trans*-($[PdCl_2\{N{=}C(R)ONC(H)CH_2CH_2CMe_2\}_2]$) 1 (R = Me, *p*-ClC$_6H_4$) were prepared by [2 + 3] cycloadditions of the corresponding organonitriles NCR (R = Me or *p*-ClC$_6$H$_4$) with a cyclic nitrone, pyrrolin *N*-oxide–($^{-}O^{+}N{=}CHCH_2CH_2CMe_2$) [7].

2.1. Preparation of the ketoimine complex 2

A solution of the oxadiazoline complex 1 (R = *p*-ClC$_6$H$_4$) (30.0 mg, 0.044 mmol) in chloroform (8 mL) was refluxed for 1 week. The reaction mixture was then dried *in vacuo*, washed with three 10 mL portions of diethyl ether and dried under air to give the final ketoimine compound 2 in high yield.

The slow and full conversion of 1 into 2 (R = *p*-ClC$_6$H$_4$) was also observed at room temperature (r.t.) for 2 months under air and without any solvent. The oxadiazoline complex 1 with an electron-donor substituent (R = Me) gives only 33% of the corresponding ketoimine derivative under the same conditions (solid state, r.t., 2 months).

Trans-($\mathbf{PdCl_2\{N(C({=}O)(R)){=}CCH_2CH_2CMe_2NH\}_2}$) 2 (R = *p*-ClC$_6H_4$). Yield: 86%. IR (cm^{-1}): 1635 (C = N), 1708 (NC = O), *ca.* 3440 (NH). ^{1}H NMR (CDCl$_3$), δ: 1.68 (s, 6H, CH$_3$), 2.05 (t, J_{HH} 7.8 Hz, 2H, CH$_2$), 3.38 (t, J_{HH} 7.8 Hz, 2H, CH$_2$), 7.19 (d, J_{HH} 8.4 Hz, 2H, CH$_{aromatic}$), 7.78 (d, J_{HH} 8.4 Hz, 2H, CH$_{aromatic}$), 10.33 (s, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 29.3 (CH$_3$), 32.9 and 34.5 (CH$_2$), 70.7 (Me$_2$C–N), 128.4, 129.3, 131.6 and 139.7 (C$_{aromatic}$), 165.9 (C = N), 182.3 (NC = O). Anal. Calcd for $C_{26}H_{30}N_4O_2Cl_4Pd$: C, 46.01; H, 4.45; N, 8.25. Found: C, 45.76; H, 4.55; N, 8.07.

2.2. Preparation of the chitosan membrane Pd-chit 1 and Pd-chit 2 catalysts

The preparation of Pd-chit 1 and Pd-chit 2 was accomplished *via* a modification of the method described by Guo [54]. A mixture of 25 mL of diluted acetic acid and 350 mg of chitosan in a two-neck flask was magnetically stirred at r.t. for 24 h. Then 50 mL of distilled water were added, to form a colloidal dispersion. Additionally, 10 mg of Pd complex 1 (R = Me) or 2 (R = *p*-ClC$_6$H$_4$) dissolved in 5 mL of chloroform were slowly added into the reaction system. A NaOH solution (0.1 mol L^{-1}) was then slowly added, until the colloidal dispersion became neutral. After stirring for 24 h, the reaction was stopped and the reaction mixture was filtered. The obtained viscous solution was cast onto a Teflon^{TM} Petri dish and allowed to stand for 96 h, at r.t. to produce a mechanically stable, light yellow, crack-free self-supported film. This membrane was washed with several solvents in the following order: chloroform, acetonitrile and methanol. The loading level of the immobilized palladium was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and shown to be *ca.* 0.16% (wt/wt) palladium on the chitosan membrane (Pd-chit 1 or Pd-chit 2), corresponding to a catalyst loading of 1.5×10^{-2} mmol palladium complex per gram of biopolymer.

2.3. Catalyst characterization

C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^{1}H and ^{13}C NMR spectra (in CDCl$_3$ or D$_2$O) were run on a Bruker Avance II 400 MHz (UltraShield^{TM} Magnet) spectrometer at room temperature (r.t.). ^{1}H, ^{13}C chemical shifts (δ) are expressed in ppm relative to Si(Me)$_4$. *J* values are in Hz. For the determination of the degree of *N*-acetylation (DA) of chitosan, 10 mg of Pd-chit 1 and Pd-chit 2 were dissolved in 1 mL HCl 1% D$_2$O (v/v) solution and stirred at room temperature for 24 h. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX and a Jasco FT/IR-430 instrument in KBr pellets and the wavenumbers are in cm^{-1}. The microwave (M.W.) irradiation experiments were undertaken in a focused M.W. CEM Discover reactor (10 mL, 13 mm diameter, 100 W) which is fitted with a rotational system and an IR detector of temperature. ICP-AES analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico.

ICP-AES analyses were performed for the pure catalysts Pd-chit 1 and Pd-chit 2 before the Suzuki–Miyaura reaction, and also for the leaching tests for both mother liquor and poly(4-vinylpyridine) (PVPy) after the catalytic run. In the case of the sample containing PVPy, it was heated over a heating plate in a porcelain crucible, in the presence of aqua regia (2 mL), four times, and the solid residue was dissolved in 0.5 M aqueous HCl. The palladium content was below the minimum ICP detection level (50 ppb of Pd, in our equipment) for both the mother liquor and poly(4-vinylpyridine).

SEM analyses were carried out by using a JEOL-JSM-6360 LV microscope operating at 12 and 20 kV, by the Department of Chemistry, FFCLRP, University of São Paulo. The observed surface was obtained by coating the cryogenic fracture with a thin gold layer. TG-DTA analyses were done under synthetic dry air (N$_2$ White Martins, flux of 100 cm^3 min^{-1}) using a SDT 2960 Simultaneous DTA-TGA from TA Instruments, at a heating rate of 10 °C/min, by the Department of Chemistry, FFCLRP, University of São Paulo.

2.4. Microwave-assisted Suzuki–Miyaura cross-coupling reaction of p-haloanisole and phenylboronic acid in water

In a typical experiment, *p*-bromoanisole (30.0 mg, 0.160 mmol), phenylboronic acid (21.5 mg, 0.176 mmol), K$_2$CO$_3$ (44.3 mg, 0.321 mmol), the phase-transfer agent tetrabutylammonium bromide TBAB (51.7 mg, 0.160 mmol), the catalyst Pd-chit 1 (8.3 mg, 1.2×10^{-4} mmol, 7.5×10^{-2} mol% Pd relatively to *p*-bromoanisole) or Pd-chit 2 (11.4 mg, 1.7×10^{-4} mmol, 10.6×10^{-2} mol% Pd relatively to *p*-bromoanisole) and water (4 mL) were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 15 min at 120 °C, whereafter the reaction mixture was poured into water (excess) and extracted with dichloromethane (3 mL × 25 mL). The organic extract was dried with MgSO$_4$, filtered and evaporated