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Research paper

Palladium(II) pyrazolyl–pyridyl complexes containing a sterically hindered N-heterocyclic carbene moiety for the *Suzuki–Miyaura* cross-coupling reaction

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ABSTRACT

Cationic palladium complexes stabilized by a tridentate neutral {N,N,C} ligand containing a sterically hindered N-heterocyclic carbene (NHC) moiety have been prepared and characterized. The nature of the anionic counterion in the palladium complex has been varied to get crystals suitable for X-ray diffraction. The square planar structure of one of these complexes along with the axial contribution of the sterically hindered NHC fragment has been confirmed by X-ray analysis. In addition, all the isolated [κ^3 -N,N,C} Pd^{II}Cl]⁺X[−] [X[−] = Cl, PF₆, BF₄, B(C₆H₃Cl₂)₄] ion pairs have been scrutinized as catalysts in the cross-coupling *Suzuki–Miyaura* reaction between phenylboronic acid and variably substituted halo-aryl acceptors. Selected issues from this series have shown improved catalyst turn-over frequencies (TOFs) with respect to structurally related catalytic systems of the *state-of-the-art*.

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1. Introduction

The design and synthesis of new ligands featured by a mixed-donor atom set and including one or more N-heterocyclic carbene (NHC) frameworks have received a great deal of attention in the last decade because of their high versatility in the fields of coordination chemistry and homogeneous catalysis [1]. The strong σ -donor and relatively weak π -acceptor properties of NHCs make them valuable mimics of phosphines in transition-metal coordination chemistry [2]. In addition, NHC frameworks generally present higher donor capability and basicity than phosphines and offer more versatility to the easy tuning of their stereo-electronic properties compared to their P-based counterparts whose manipulation is often not trivial [3]. In this paper, a highly sterically hindered NHC group has been selected as the third donor site for the construction of a tridentate pyrazolyl–pyridyl ligand [L_{(N,N,C)}}] containing a hemilabile coordinative arm (N-pyrazole) (Scheme 1) [4–8].

From a homogeneous catalysis viewpoint, the ligand hemilability provides access to a vacant coordination site at the metal center

and facilitates an effective coordination, activation and transformation of the substrate. The neutral [L_{(N,N,C)}}] ligand has been used to synthesize a series of Pd(II) complexes to be used in turn as pre-catalysts for the cross-coupling reaction between an organoboron reagent and an organic halide (*Suzuki–Miyaura* cross coupling) [9]. The strong σ -donor character of NHC *trans* to the N-pyrazole is thought to speed up the N-dissociation (*trans effect*), thus making this coordinative position more reactive in the interaction with the substrate throughout the catalytic process. Structurally related ligands featuring with the same donor atom set but containing less sterically demanding substituents at the NHC fragment have been discussed in the literature and scrutinized in combination with a Pd(II) precursor for the *Suzuki–Miyaura* cross-coupling [10]. This reaction consists of three consecutive steps in the catalytic cycle: the substrate oxidative addition, an aryl transmetalation from boron to palladium and the final product reductive elimination [11]. Overall, the process benefits from the use of electron-donating and sterically demanding ligands for promoting the first and last steps, respectively [9,12]. Herein, we describe the methodology applied for the synthesis of a sterically hindered imidazolium salt as precursor of the neutral [L_{(N,N,C)}}] ligand and the isolation and characterization of cationic Pd(II) complexes with different counterions. The effect of bulky substituents on NHC-based palladium complexes has important precedents in the literature,

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