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(IPr)Pd(pydc) (pydc = pyridine-2,6-dicarboxylate) – A highly active precatalyst for the sterically hindered C–N coupling reactions

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ABSTRACT

A new class of well-defined NHC–Pd complexes incorporating a pyridine-2-carboxylate or pyridine-2,6-dicarboxylate ligand has been synthesized. These novel complexes exhibited prominent catalytic activity in the sterically hindered C–N coupling reactions at elevated temperature, but relatively inferior reactivity at low temperature. The distinctly different reactivity of these NHC–Pd complexes was presumed to be associated with their unique structures of ancillary ligands.

1. Introduction

The use of *N*-heterocyclic carbenes (NHCs) as supporting ligands in the palladium-mediated homogeneous catalysis has witnessed an impressive progress over the past decade [1,2]. To date, a great number of the structurally diverse NHC-containing palladium complexes have been prepared and characterized. These prevailing NHC–Pd complexes have proven to be exceedingly versatile and robust precatalysts in the widespread C–C, C–heteroatom bond-formation reactions [3]. Due to stronger σ-donor property of NHCs [4], air- and moisture-stability, easy handling, and ready structure modification, well-defined monoligated NHC–Pd(II) complexes [2f,2g,2l] have shown superior catalytic reactivity relative to the bulky tertiary phosphine/Pd systems [5], especially in the field of Pd-catalyzed cross-coupling reactions. Generally, they consist of an accurate 1:1 ratio of Pd/NHC (Scheme 1) that avoid the use of excess costly ligand and, more important, usually exhibit enhanced reactivity associated with easy activation to a highly active low-coordinate [LPd^0] species [6].

The catalytic activity of these NHC–Pd complexes significantly related to the NHC and other ancillary ligands around Pd center. In a series of investigation, Nolan, Glorius, and Organ have demonstrated that the reactivity profile of NHC–Pd complexes related substantially to the steric nature of *N*-substituent groups R in the NHC backbone [7–10]. Meanwhile, except for the dominant NHC ligand, other ancillary ligands around the palladium center also play a very crucial role to their catalytic performance. By replacement of the allyl group with the cinnamyl group in (NHC)Pd(allyl)Cl complexes, in 2006 Nolan developed a new class of precatalysts with enhanced catalytic activity which probably resulted from an accelerated activation step from the corresponding NHC–Pd(II) complex to the active [(NHC)Pd^0] species [11]. Conversely, a dramatic reduction of catalytic activity was discovered by Organ when using more electrophilic 2,6-lutidine instead of 3-chloropyridine in the precatalysts of PEPPSI family [10]. A balance of the pyridine ligand detaching from and reattaching to the [NHC–Pd^0] complex in solution was thus implied. Moreover, Nolan discovered in the type of (NHC)Pd(acac)Cl (acac = acetylacetonato) complexes that various substituted patterns in the acac group would give rise to the distinctly different reactivity [12]. Recently, we also observed that the steric and electronic nature of the sal (sal = salicylaldimine) ligand in the (NHC)Pd(sal)Cl complexes showed a significant effect on their catalytic performance [13]. Incorporating the electron-withdrawing group(s) into *N*-substituted aryl group in the sal unit would led to the extremely increased reactivity in the amination reactions of aryl chlorides. More recently, Navarro reported a new family of complexes (NHC)PdCl$_2$(tea) using intermediate σ-donor capability triethylamine (tea) as a "throw-away" neutral ligand [14]. These complexes exhibited higher catalytic activity at lower temperature than the corresponding 3-chloropyridine counterparts.

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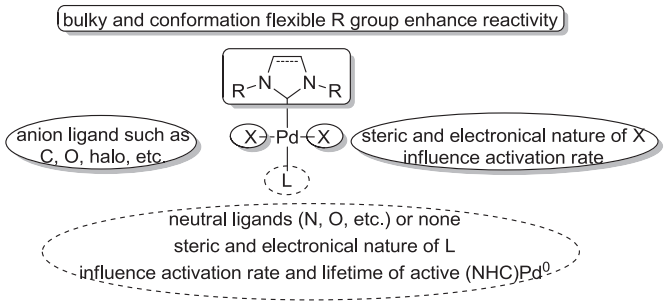


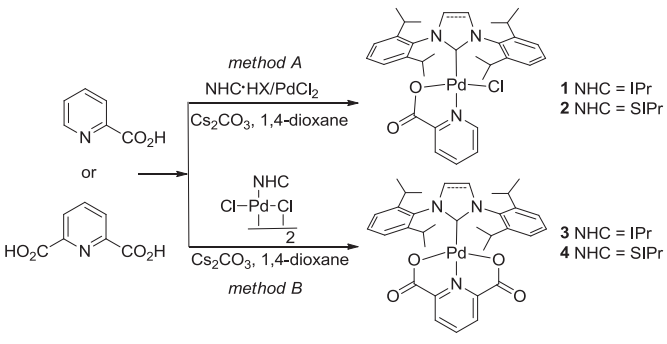
Scheme 1. Well-defined monoligated NHC–Pd(II) complexes.

As part of our ongoing project aimed to explore new types of well-defined NHC–Pd complexes with improved catalytic profiles, we envision incorporation of a pyridine-2-carboxylate (pyc) or pyridine-2,6-dicarboxylate (pydc) [15] anion ligand into the NHC–Pd(II) complex to form a new class of [O,N] or [O,N,O] chelate NHC–Pd complexes. Organ and co-workers have discovered in the PEPPSI catalyst family that, as an ancillary ligand, substituted pyridine played an extremely important role in the activation of precatalyst [10]. 2,6-Lutidine instead of 3-chloropyridine retarded greatly the disassociation rate of ancillary ligand. We also observed in the (NHC)Pd(sal)Cl complexes that the decreased strength of the Pd–N bond led to easier activation of the complex [13]. As a result, the presence of electron-withdrawing carboxylate group(s), decreasing greatly the charge density of pyridine ring, may cause a weakened N–Pd coordination which facilitates disassociation of ancillary ligand from the Pd center and accelerated formation of the active [(NHC)Pd^0] species.

2. Results and discussion

2.1. Synthesis of (NHC)Pd(pyc)Cl and (NHC)Pd(pydc) complexes

We therefore commenced synthesizing well-defined NHC–Pd complexes **1**–**4** (Scheme 2). Initially, using the protocol analogous to Organ's procedure [16], these NHC–Pd complexes were prepared from salts NHC·HX and $PdCl_2$ in a straightforward one-pot procedure (*method A*). For picolinate-containing complexes **1** and **2**, modest to good yields were obtained under the standard reaction conditions. However, with the sterically encumbered pyridine-2,6-dicarboxylic acid, reaction only gave the desired precatalysts **3** and **4** in poor yields along with remarkable degraded Pd black. As a result, an alternative, more efficient synthetic method was pursued for improving yields. To our delight, through straightforward cleavage of the [NHC–$PdCl_2$] dimers with two equivalents of 2-picolinic acid or pyridine-2,6-dicarboxylic acid in the presence of a base (*method B*), the desired NHC–Pd complexes **1**–**4** could also be obtained in satisfied yields [17]. The requisite [NHC–$PdCl_2$] dimers could be conveniently prepared from $Pd(OAc)_2$ [8], $(PhCN)_2PdCl_2$ [18], or [Pd(η^3-allyl)Cl]$_2$ [19]. The structures of all four complexes were fully characterized by means of elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and ESI-MS. These complexes commonly exhibit high air- and moisture-stability, allowing for indefinite storage and easy handling on the benchtop.



Scheme 2. Synthesis of NHC–Pd complexes **1**–**4**.

2.2. X-ray crystal structures of (NHC)Pd(pyc)Cl and (NHC)Pd(pydc) complexes

Suitable crystals for single-crystal diffraction analyses of (NHC)Pd(pyc)Cl and (NHC)Pd(pydc) complexes **1**–**4** were obtained by slow diffusion of *n*-pentane into dichloromethane solution (Figs. 1 and 2). Selected bond lengths and angles for compounds **1** and **3** were listed in the captions for figure, respectively. The crystal structures revealed unambiguously a [O,N] bidentate chelate coordination in complexes **1** and **2**, and a slightly distorted square-plane geometry around the palladium center. Like the precatalysts of the PEPPSI family [9,10,16], the neutral σ-donating pyridine nitrogen atom is located *trans* to the NHC ligand, while the carboxylate oxygen anion is situated in the *cis* to the NHC ligand in a direction opposite the chloride anion. While in complexes **3** and **4**, a unique [O,N,O] tridentate *trans*-chelating planar configuration was observed. From the crystal X-ray diffraction data, due to induction by [O,N,O] tridentate chelating coordination of pyridine-2,6-dicarboxylate, the distances of the Pd–$C_{carbene}$ bonds in complexes **3** and **4** are 2.005 Å and 1.996 Å in solid crystals, respectively, which are obviously larger than those of complexes **1** and **2** (1.963 Å for **1** and 1.970 Å for **2**, respectively). In addition, the Pd–$C_{carbene}$ bonds of complexes **3** and **4** are also comparatively longer than those of NHC–Pd complexes [(IPr)$PdCl_2]_2$ dimer [18b] and (IPr)Pd(3-chloropyridine)Cl_2 [10] (1.9553 Å and 1.962 Å, respectively). Generally, the longer Pd–$C_{carbene}$ bond facilitated oxidative addition of [(NHC)Pd^0] species to the sterically encumbered electrophile

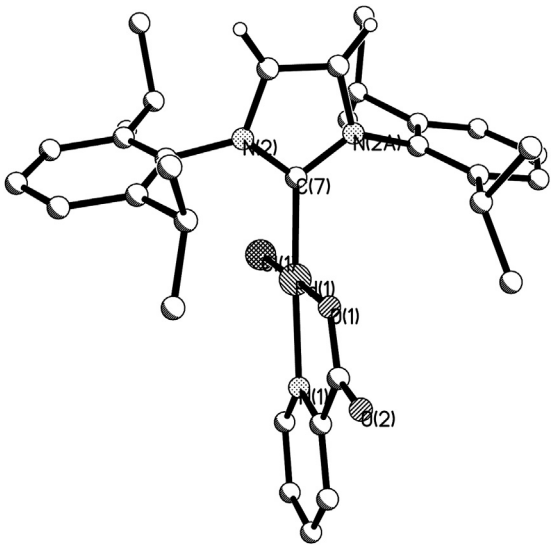


Fig. 1. Crystal structure of complex **1** with thermal ellipsoids drawn at the 50% probability level and most H atoms (except those in the backbone of NHC) and co-crystallizing solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(7) 1.963(2), Pd(1)–O(1) 2.0219(17), Pd(1)–N(1) 2.067(2), Pd(1) –Cl(1) 2.2773(7); O(1)–Pd(1)–N(1) 81.59(8), O(1)–Pd(1)–Cl(1) 178.39(5), C(7)–Pd(1)–O(1) 89.84(8), N(1)–Pd(1)–Cl(1) 96.80(6), N(2)–C(7)–N(2A) 105.39(19), O(1) –Pd(1)–N(1) 81.59 (8).