

# SYNLETT Spotlight 161

## *trans*-Dichloro-bis(benzonitrile)palladium(II): A Versatile Reagent in Organic Synthesis

Compiled by Sulagna Brahma



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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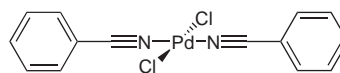
### Introduction

The use of Pd(II) complexes as catalysts in organic reactions has been well-established since the beginnings of organic synthesis. Due to its versatility, *trans*-dichloro-bis(benzonitrile)palladium(II) receives special attention as activating agent and also as stabilizing agent. Recently, Khinast and his coworkers reacted ligands like (*N*-[3-(trimethoxysilyl)propyl]ethylenediamine, 2-(2'-pyridyl)ethyltrimethoxysilane, etc. with Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> to prepare immobilized catalysts with improved activity in Suzuki coupling reactions.<sup>1</sup> The presence of polar groups in the ligand can increase the interaction of the metal complexes with a substrate which is able to improve enantioselectivity in asymmetric catalysis.<sup>2</sup> With this aim Condom et al. used Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> for the synthesis of the new asymmetric, water-soluble phosphine (*S*)-(-)-(3-diphenylphosphino-2-hydroxy-propyl)trimethylammonium chloride from the accessible (*S*)-(-)-(3-chloro-2-hydroxypropyl)trimethylammonium chloride.<sup>3</sup>

Various fluorinated arene ligands based on diimine and diacetylpyridine backbones, synthesized using Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>, serve as precursor compounds for the investigations of  $\pi$ -stacking interaction. Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> is suitable for single-crystal X-ray diffraction studies, obtained by the growth from solution in benzonitrile, as it readily loses benzonitrile to form the cubic cluster Pd<sub>6</sub>Cl<sub>12</sub>, which co-crystallizes with a variety of planar aromatic hydrocarbons.<sup>4</sup>

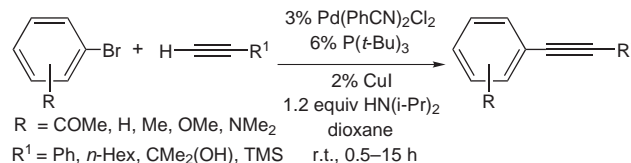
Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> appears to be a versatile activating agent for the alcoholic and epoxide functionality under unusually mild conditions.<sup>5</sup> Another important aspect of this reagent is that it can be used as stabilizing agent for unstable azirine compounds via formation of 1:2 and 1:1 complexes.<sup>6</sup>

This reagent is generally prepared by condensation of PdCl<sub>2</sub> in benzonitrile and it is also commercially available.

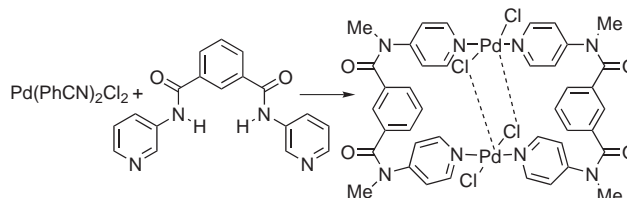


### Abstracts

(A) Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> in combination with P(*t*-Bu)<sub>3</sub>, indeed a highly active catalyst for Sonogashira couplings, provides a mild, efficient and general method for the reaction of aryl bromides at room temperature.<sup>7</sup> Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>/P(*t*-Bu)<sub>3</sub> can even effect Sonogashira coupling of hindered aryl bromides.



(B) Reaction of Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> with the ligand LL [3-C<sub>6</sub>H<sub>4</sub>(CONMe-4-C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] gave the neutral dipalladium(II) macrocycle *trans,trans*-[Pd<sub>2</sub>Cl<sub>4</sub>( $\mu$ -LL)<sub>2</sub>], with a short separation between the palladium atoms of the lantern complex [Pd<sub>2</sub>( $\mu$ -LL)<sub>4</sub>]<sup>4+</sup>, which acts as a host for chloride ions and forms the complex [Pd<sub>2</sub>( $\mu$ -Cl)( $\mu$ -LL)<sub>4</sub>]<sup>3+</sup>, in which the distance between the palladium atoms is significantly larger [Pd-Pd = 6.56 Å].<sup>8</sup>



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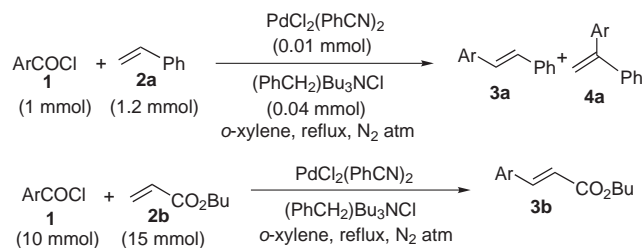
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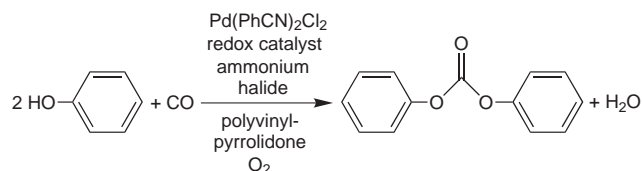
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(C) Miura's group reacted various aryl chlorides (**1**) with styrene (**2a**) in the presence of the catalyst system Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>/(PhCH<sub>2</sub>)<sub>3</sub>NCl to give the corresponding stilbene derivatives **3a** in satisfactory yields.

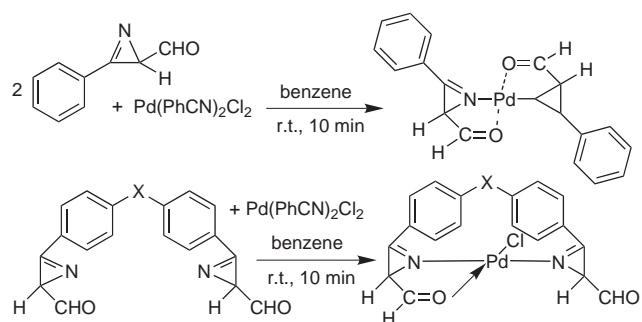
The aryl chlorides **1** also reacted with butyl acrylate (**2b**) to afford butyl (*E*)-cinnamate and its derivatives (**3b**) in 79–95% yields.<sup>9</sup>



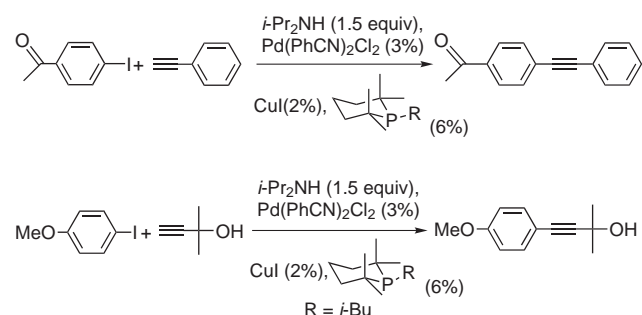
(D) Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> in the presence of polyvinylpyrrolidone (PVP) as a polymer support is an efficient catalyst for the direct synthesis of diphenyl carbonate (DPC) via oxidative carbonylation of phenol using carbon monoxide and air. This is the first example of the successful usage of polymer support in the oxidative carbonylation yielding DPC.<sup>10</sup>



(E) Recently Ray et al. used Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> to stabilize azirines containing an aldehyde functionality via the formation of 2:1 and 1:1 complexes.<sup>11</sup>



(G) The group of McNulty and Capretta described the synthesis of a small library of phosphorinanes and demonstrated their utility in cross-coupling chemistry using Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>. The phosphorinanes allowed for modification of one of the alkyl moieties permitting steric and electronic fine-tuning of the ligands. In addition, optimization revealed that Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> was the best palladium source for these couplings.<sup>12</sup>



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