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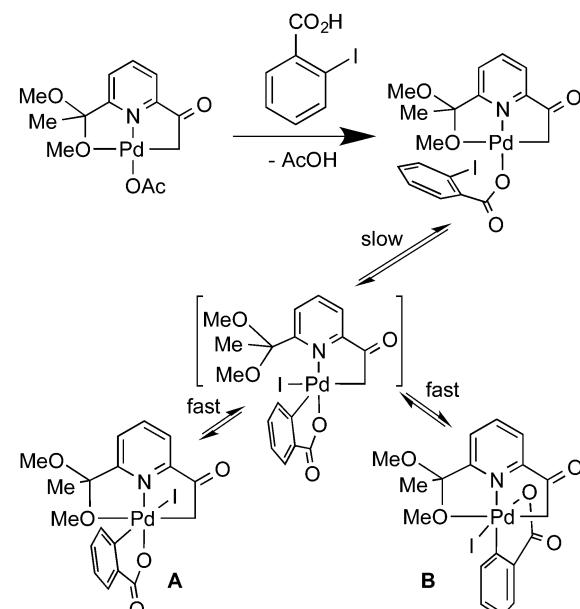
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Oxidative addition of *N*-(2-iodophenyl)formamide to $\text{Pd}(\text{dba})_2$ (dba = dibenzylideneacetone) in the presence of 4,4'-ditertbutyl-2,2'-bipyridine ('Bubpy) produces $[\text{Pd}(\text{C}_6\text{H}_4\text{NHCHO}-2)\text{I}(\text{'Bubpy})]$ (1) which inserts 2-iodophenyl isocyanide to give $[\text{Pd}\{\text{C}(\equiv\text{NC}_6\text{H}_4\text{I}-2)\text{C}_6\text{H}_4\text{NHCHO}-2\}\text{I}(\text{'Bubpy})]$ (2). Dehydroiodination of 2 with $\text{Ti}(\text{acac})_4$ (acacH = acetylacetone) gives the stable $\text{Pd}(\text{iv})$ complex OC-6-35- $[\text{Pd}\{\text{C},\text{N},\text{N}-\text{C}(\equiv\text{NC}_6\text{H}_4\text{I}-2)\text{C}_6\text{H}_4\text{NCHO}-2\}\text{I}(\text{'Bubpy})]$ (4) likely resulting from the spontaneous oxidative addition of the $\text{I}-\text{Ar}$ moiety present in the unstable intermediate $\text{Pd}(\text{ii})$ complex $[\text{Pd}\{\text{C},\text{N}-\text{C}(\equiv\text{NC}_6\text{H}_4\text{I}-2)\text{C}_6\text{H}_4\text{NCHO}-2\}\text{I}(\text{'Bubpy})]$ (3). The crystal structure of 4 shows various $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds resulting in chains of dimers stacked along the a axis.

The important role of Pd -catalyzed $\text{C}-\text{C}$ cross coupling reactions in organic synthesis is very well known.¹ These reactions involve $\text{Pd}(0)^{2,3}$ or $\text{Pd}(\text{ii})^4$ precatalysts and, in most cases, the catalyst is Pd metal or a $\text{Pd}(0)$ complex formed from the precatalyst. However, in some cases in which the precatalyst is a $\text{Pd}(\text{ii})$ complex, experimental^{3,5,6} and theoretical⁷ studies suggested a $\text{Pd}(\text{ii})/\text{Pd}(\text{iv})$ catalytic cycle as an alternative to the usual $\text{Pd}(0)/\text{Pd}(\text{ii})$ one. The main objections to this proposal, when an aryl halide is involved (Heck, Suzuki–Miyaura, Sonogashira, Stille, *etc.* coupling reactions), were that (1) the necessary oxidative addition of the haloarene to $\text{Pd}(\text{ii})$ had no experimental support, and (2) the $\text{Pd}(\text{iv})$ intermediate formed during catalysis had not been detected. However, we have recently given experimental evidence against these two objections by isolating the $\text{Pd}(\text{iv})$ oxidative addition product (**A**, Scheme 1) of an aryl iodide to a $\text{Pd}(\text{ii})$ complex,^{8,9} and detecting the $\text{Pd}(\text{iv})$ complex in a Heck-type catalytic reaction.¹⁰

The easy formation of complexes **A** and **B** (Scheme 1) was explained as a consequence of the coordination of the


 Scheme 1 Synthesis of complex **A**.

2-iodobenzoato ligand that would bring the iodine and Pd atoms close to each other.⁹ We have used the same coordination-assisted oxidative addition of the 2-iodobenzoato ligand with other $\text{Pd}(\text{ii})$ complexes.⁸

In this work we describe a new way of assistance of the oxidative addition of an aryl halide to a $\text{Pd}(\text{ii})$ complex. It involves the insertion of an isocyanide into the $\text{Pd}-\text{C}$ bond of an aryl $\text{Pd}(\text{ii})$ complex (**1** in Scheme 2), a very well known process¹¹ that has been recently reviewed.¹² The rising interest of $\text{Pd}(\text{iv})$ chemistry in synthesis and catalysis is very well established.¹³

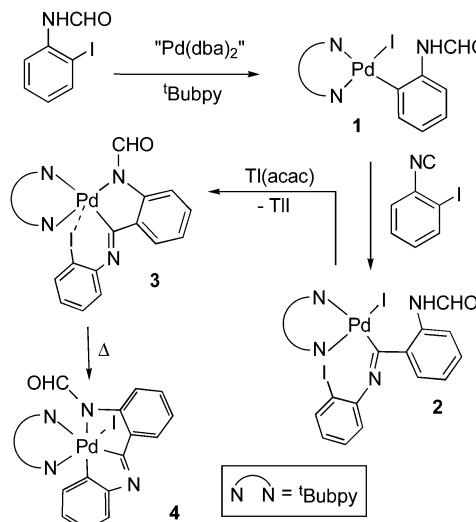
Complex **1** (Scheme 2) was obtained by the oxidative addition of *N*-(2-iodophenyl)formamide¹⁴ to $\text{Pd}_2(\text{dba})_3\cdot\text{dba}$ (" $\text{Pd}(\text{dba})_2$ ", dba = dibenzylideneacetone) in the presence of 'Bubpy' (1:1:1, toluene, room temperature, 5 h, 80%). Insertion of 2-iodophenyl isocyanide into the $\text{Pd}-\text{C}$ bond of **1** produced the iminobenzoyl complex **2** (1:1, CH_2Cl_2 , room temperature, 20 min, 89%)

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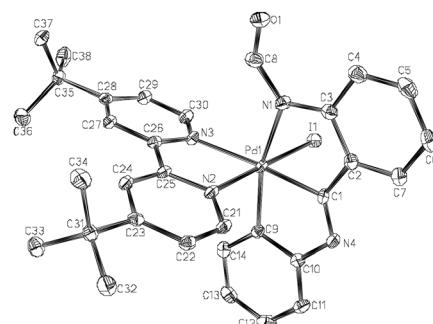


Scheme 2 Synthesis of complex 4.

which decomposed upon heating in solution or even upon standing at room temperature to give the almost quantitative amount of $[\text{PdI}_2(\text{t-Bubpy})]$ along with an unresolved mixture of products. This result suggested that an unstable diiodopalladium(IV) complex, probably $[\text{Pd}\{\text{C},\text{N},\text{N}-\text{C}(=\text{N}_\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NHCHO-2})\}_2\text{I}_2(\text{t-Bubpy})]$, formed from the oxidative addition to $\text{Pd}(\text{II})$ of the I-iminobenzoyl fragment. The great instability of the only known diiodo $\text{Pd}(\text{IV})$ organometallic complex has been previously reported.¹⁵ In order to avoid this decomposition process we decided to dehydroiodinate complex 2 with $\text{Ti}(\text{acac})$ (acacH = acetylacetone) but, instead of the expected complex 3, spontaneous formation of the $\text{Pd}(\text{IV})$ complex 4 occurred, containing a stabilizing^{6,16} pincer ligand. The isolated reaction mixture (1:1, acetone, 1 h, room temperature) was shown by ^1H NMR to contain mainly 4, while intermediate 3, which we assume to be a minor component of the mixture, could not be isolated even from a 15 min reaction. Pure complex 4 was isolated in 75% yield at 50 °C for 5 h but also after a couple of days standing at room temperature.

The oxidative addition reactions of R-X (R = alkyl) compounds to $\text{Pd}(\text{II})$ complexes lead to *cis*-, *trans*- or mixtures of both $\text{Pd}(\text{IV})$ isomers depending on the nature of R .¹⁷ In the case of the oxidative addition of 2-iodobenzoate (Scheme 1), the ^1H NMR spectrum of the reaction mixture showed an equilibrium between both isomers A and B, the later characterized by X-ray crystallography. The presence of a weakly coordinating group (MeO) may be responsible for the easy conversion of both isomers through a pentacoordinate intermediate,⁹ which in the present case seems not to be available (even at 50 °C for 5 h) since both the 'Bubpy' and the C^{N} ligands form robust palladacycles. Therefore, the results of the three known reported cases suggest that the intramolecular oxidative addition of aryl iodides to $\text{Pd}(\text{II})$ leads to the *cis* isomer that can isomerize to the *trans* isomer if a weakly coordinating group facilitates the process.

According to NMR data, complexes 1 and 2 form as mixtures of isomers as is also the case of the starting compound $\text{N}-(2\text{-iodophenyl})\text{formamide}$.^{14,18}

Fig. 1 Ortep drawing (50% probability ellipsoids) of complex 4· CH_2Cl_2 .

The crystal structure of 4· CH_2Cl_2 (Fig. 1) has been determined by X-ray diffraction methods. It shows the Pd atom in a rather distorted octahedral environment. The greater *trans* influence of carbon with respect to nitrogen donor ligands is observed in the $\text{Pd}-\text{N}_{\text{t-Bubpy}}$ bond distances (2.1763(18) \AA vs. 2.0767(19) \AA). The $\text{Pd}-\text{I}$ bond distance (2.5992(3) \AA) is similar to that in the only other moniodo $\text{Pd}(\text{IV})$ complex structurally characterized having iodo *trans* to nitrogen (2.5902(3) \AA).¹⁹ A chain of dimers forms along the a axis through various $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Very few crystal structures of $\text{Pd}(\text{IV})$ -iodo complexes have been reported, namely those of one triiodo²⁰ and three monoiodo^{9,19,21} derivatives.

In conclusion, we show an alternative way to oxidatively add an iodoarene to a $\text{Pd}(\text{II})$ complex to give a very stable aryl $\text{Pd}(\text{IV})$ complex through insertion of 2-iodophenyl isocyanide into the C-Pd bond of an aryl $\text{Pd}(\text{II})$ complex. This work opens a new research line that, provided the appropriate aryl $\text{Pd}(\text{II})$ complexes and 2-iodaryl isocyanides (or related reagents) were used, could lead to interesting organic products through unstable $\text{Pd}(\text{IV})$ intermediates.

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