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Chemical Communications

COMMUNICATION

A New Type of Oxidative Addition of an Iodoarene to a Pd(II) Complex

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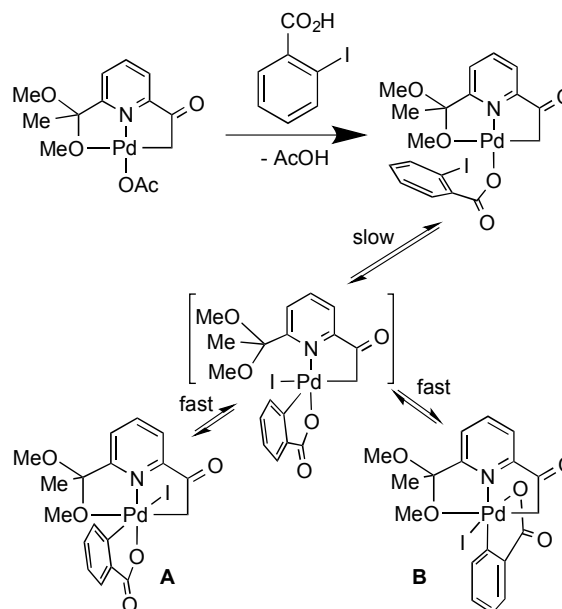
Abstract: Oxidative addition of N-(2-iodophenyl)formamide to Pd(dba)₂ (dba = dibenzylideneacetone) in the presence of 4,4'-ditertbutyl-2,2'-bipyridine (¹Bubpy) produces [Pd(C₆H₄NHCHO-2)](¹Bubpy) (**1**) which inserts 2-iodophenyl isocyanide to give [Pd{C(=NC₆H₄I-2)C₆H₄NHCHO-2}](¹Bubpy) (**2**). Dehydroiodination of **2** with Tl(acac) (acacH = acetylacetonate) gives the stable Pd(IV) complex OC-6-35-[Pd{C,N,N-C(=NC₆H₄-2)C₆H₄NHCHO-2}](¹Bubpy) (**4**) likely resulting from spontaneous oxidative addition of the I-Ar moiety present in the unstable intermediate Pd(II) complex [Pd{C,C,N-C(=NC₆H₄I-2)C₆H₄NHCHO-2}](¹Bubpy) (**3**). The crystal structure of **4** shows various C-H...O hydrogen bonds resulting in chains of dimers stacked along the *a* axis.

The important role of Pd-catalyzed C–C cross coupling reactions in organic synthesis is very well known.¹ These reactions involve Pd(0)^{2,3} or Pd(II)⁴ precatalysts and, in most cases, the catalyst is Pd metal or a Pd(0) complex formed from the precatalyst. However, in some cases in which the precatalyst is a Pd(II) complex, experimental^{5,6} and theoretical⁷ studies suggested a Pd(II)/Pd(IV) catalytic cycle as an alternative to the usual Pd(0)/Pd(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 Pd(II) had not experimental support, and (2) the Pd(IV) intermediate formed during catalysis had not been detected. However, we have given recently experimental evidences against these two objections by isolating the Pd(IV) oxidative addition product (**A**, Scheme 1) of an aryl iodide to a Pd(II) complex,^{8,9} and detecting the Pd(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 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 Pd(II) complex.⁸

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



Scheme 1. Synthesis of complex A.

Complex **1** (Scheme 2) was obtained by the oxidative addition of N-(2-iodophenyl)formamide¹⁴ to Pd₂(dba)₃·dba ("Pd(dba)₂", dba = dibenzylideneacetone) in the presence of ¹Bubpy (1:1:1, toluene, room temperature, 5 h, 80%). Insertion of 2-iodophenyl isocyanide into the Pd–C bond of **1** produced the iminobenzoyl

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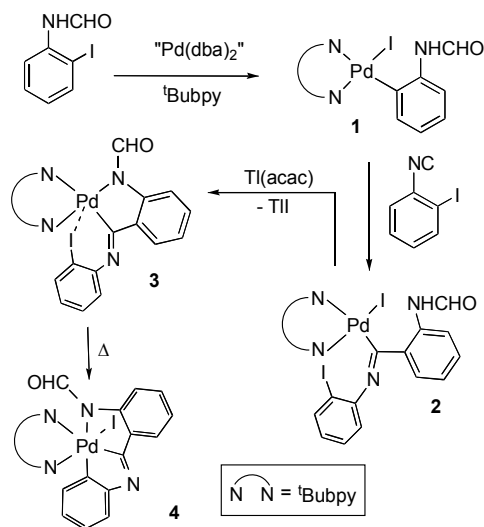
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complex **2** (1:1, CH₂Cl₂, room temperature, 20 min, 89%) which decomposed upon heating in solution or even on standing at room temperature to give the almost quantitative amount of [Pd]₂(^tBubpy)] along with an unresolved mixture of products. This result suggested that an unstable diiodopalladium(IV) complex, probably [Pd(C(=NC₆H₄-2)C₆H₄NHCHO-2)]₂(^tBubpy)] formed from the oxidative addition to Pd(II) of the I-iminobenzoyl fragment. The great instability of the only known diiodo Pd(IV) organometallic complex has been previously reported.¹⁵ In order to avoid this decomposition process we decided to dehydroiodinate complex **2** with Ti(acac) (acacH = acetylacetonate) but, instead of the expected complex **3**, spontaneous formation of the Pd(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 the 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 Pd(II) complexes lead to cis-, trans- or mixtures of both Pd(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 during 5h) since both the ^tBubpy 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 Pd(II) lead to the cis isomer that can isomerize to the trans isomer if a weakly coordinating group facilitates the process.



Scheme 2. Synthesis of complex **4**

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

The crystal structure of **4**·CH₂Cl₂ (Figure 1) has been determined by X-ray diffraction methods. It shows the Pd atom in an rather distorted octahedral environment. The greater *trans influence* of carbon with respect to nitrogen donor ligands is observed in the Pd–N_{tBubpy} bond distances (2.1763(18) vs 2.0767(19) Å). The Pd–I bond distance (2.5992(3) Å) is similar to that in the only other monoiodo Pd(IV) complex structurally characterized having iodo trans to nitrogen (2.5902(3) Å).¹⁹ A chain of dimers forms along the a axis through various C–H...O hydrogen bonds.

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

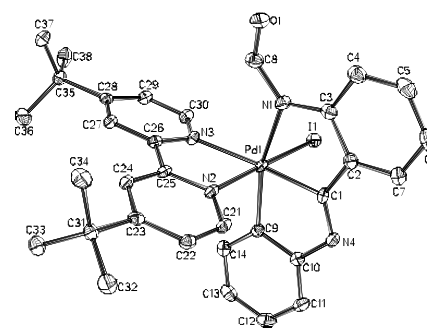


Figure 1. Ortep drawing (50% probability ellipsoids) of complex **4**·CH₂Cl₂.

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

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