Research paper

Reaction of arylhydroxylamines with [Pd(Neoc)(NO$_3$)$_2$] (Neoc = neocuproine). Non-innocent behavior of the nitrate anion

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ABSTRACT

In an effort to understand the first stages of the reduction of nitroarenes to anilines by palladium/phenanthroline complexes and suspecting that arylhydroxylaminato complexes may be intermediates in this process, we investigated the reactivity of [Pd(Neoc)(NO$_3$)$_2$] (Neoc = neocuproine = 2,9-dimethyl-1,10-phenanthroline) with 3,5-dichlorophenylhydroxylamine. Spectroscopic evidence indicates that the desired [Pd(Neoc)(ONHC$_6$H$_3$Cl$_2$)(NO$_3$)] is indeed formed, but the complex is not stable and decomposes within a few hours. Two of the decomposition products were characterized by single crystal X-ray diffraction. They are a N-aryl-N-nitrosohydroxylaminato complex, [Pd(Neoc)(ON(3,5-C$_6$H$_3$Cl$_2$)NO)][NO$_3$] (major decomposition product) and a nitro-nitrate complex [Pd(Neoc)(NO$_2$)(NO$_3$)]. The results indicate that the nitrate ion is not innocent in the starting complex and oxidize hydroxylamine, being reduced itself to NO$_2^-$ and NO.

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1. Introduction

Carbonylation reactions of nitroarenes to give isocyanates, carbamates and ureas constitutes one of the most promising alternatives to the use of phosgene for the industrial production of these key intermediates [1–5]. The reaction is catalyzed under homogeneous conditions by many different transition metal complexes, among which the most actively investigated are based on palladium, rhodium or ruthenium. For all of the catalytic systems most active in this transformation, it has been proven that the nitroarene is intermediately reduced to the corresponding arylamine and only at a later stage the latter is carbonylated [6–18]. It is generally agreed that the nitroarene is reduced by CO to the corresponding nitrosoarene, which should remain bound to the metal, either in an η$_2$ complex [19] or as part of a metallacycle that also includes CO and/or CO$_2$ [8,9,20–24]. Although "on paper" it is easy to draw mechanisms that lead to the direct evolution of aryl isocyanates from the isolated metallacycles, this does not appear to be a possible, or at least a catalytically relevant pathway. The isolated ruthenium [20] and rhodium [8,9] metallacycles are stable in a CO

atmosphere, but decompose quickly in the presence of a proton source, even a weak one like an alcohol, to generate arylamines. Even if the palladium metallacycle appears to be able to generate isocyanates under forcing conditions, kinetic measurements clearly show that in the presence of alcohols or amines, this constitutes at most a very minor pathway, most of the nitroarene being again intermediately transformed into an arylamine [17,18]. The steps leading from arylamine to carbonylated products have been investigated in some depth both with ruthenium-DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane) [6,7] and palladium-phenanthroline [18] complexes and, at least in these cases, are relatively well understood. However, virtually nothing is known on how arylamines are formed from the initial nitrosoarene complexes. Imido (nitrene) complexes have often been proposed to be intermediates in the reaction, especially in the older literature, but no strong evidence in favor of an active role of such species in the reactions has ever been obtained. In some cases, it has been shown that trinuclear ruthenium or iron imido complexes previously supposed to play an active role in the formation of isocyanates or amines from nitroarenes, actually play no role in such transformations [12,13,25,26]. In recent years, we have focused our attention on palladium-phenanthroline catalysts because these systems are the most active for the carbonylation of nitroarenes to give carbamates or ureas [14–17,27–32]. During our studies we evidenced that the addition of acids increases the

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selectivity towards carbonylated products, whereas the presence of bases, even a large excess of basic phenanthroline ligands, boosts the formation of azo- and azoxyarenes as byproducts. Since carbonylated products derive from intermediately formed arylamines, one role of the acid may be that of influencing the formation of the latter. On the other hand, the addition of bases has a positive effect on the outcome of several reactions in which an intermediately formed nitrosoarene couples with an unsaturated group and its complete reduction to aniline must be avoided [33,34].

A simplified reaction scheme leading from a nitrosoarene complex to aniline in the presence of CO and an acid is shown in Scheme 1. More possibilities can be envisaged if one considers that the acid counteranion may attack a coordinated CO rather than directly the metal.

Very few palladium complexes featuring structure **A** are known [35–37], none with nitrogen ligands. A nickel complex featuring structure **B** has been very recently reported [38], but we are not aware of any palladium complex with this structure. However, the idea that the nitrogen ligand in an $[L_nPd(\eta_2\text{-ArNO})]$ complex has a tendency to interact with other electrophilic centers even without disrupting its η_2 coordination to palladium is supported by the existence of several polynuclear complexes in which the nitrosoarene is bridging two palladium atoms in a η_2-η_1 way [39,40]. We are also not aware of any palladium complex having a η^1–ONHAr ligand like in structure **C**. However, this kind of ligand is known for other metals [41].

Several attempts in our group to synthesize a palladium-phenanthroline nitrosoarene complex (type **A** complex in Scheme 1) by reaction of palladium(0) phenanthroline complexes with nitrosoarenes always yielded insoluble polymeric materials. The only indication on the composition of the product of the reaction between [Pd(Phen)(dba)] (dba = dibenzylideneacetone) and PhNO is the elemental analysis, indicating a composition [Pd$_2$(Phen)$_2$(PhNO)$_3$]$_n$ [42,43]. Thus, we tried to isolate putative intermediates **B** or **C** in Scheme 1 by reaction of a palladium(II) phenanthroline complex with an arylhydroxylamine rather than from a palladium(0) complex and a nitrosoarene. As a starting point we used a complex of 2,9-dimethyl-1,10-phenanthroline (neocuproine, Neoc) rather than one of simple phenanthroline because this ligand previously allowed us to observe, and even isolate, some intermediate complexes that could not be directly observed when using unsubstituted phenanthroline as the ligand [18,29]. Nitrate was employed as the anion because this is the least coordinating anion among those which allow the synthesis of a complex with composition [Pd(Neoc)X$_2$] [44,45]. With even less coordinating anions, e.g. BF$_4^-$, only complexes of composition [Pd(Neoc)$_2$][X]$_2$ can be obtained and we deemed that substitution of a chelating nitrogen ligand in these systems may be more difficult. However, we found nitrate not to be an innocent anion/ligand during the reaction and some unexpected results have been obtained that will be described in this work.

2. Results and discussion

2.1. Reactions of [Pd(Neoc)(NO$_3$)$_2$] with 3,5-dichlorophenylhydroxylamine

3,5-Dichlorophenylhydroxylamine was chosen as a reagent because it is our and others experience that the presence of chlorine atoms on the aryl ring stabilizes complexes related to those expected in this work and, most importantly, affords complexes that crystallize more easily [9,19]. [Pd(Neoc)(NO$_3$)$_2$] (**1**) is almost insoluble in CH$_2$Cl$_2$, but dissolves quickly upon addition of 3,5-Cl$_2$-C$_6$H$_3$NHOH. At least two equivalents of hydroxylamine are required to complete the reaction, otherwise undissolved **1**

Scheme 1.
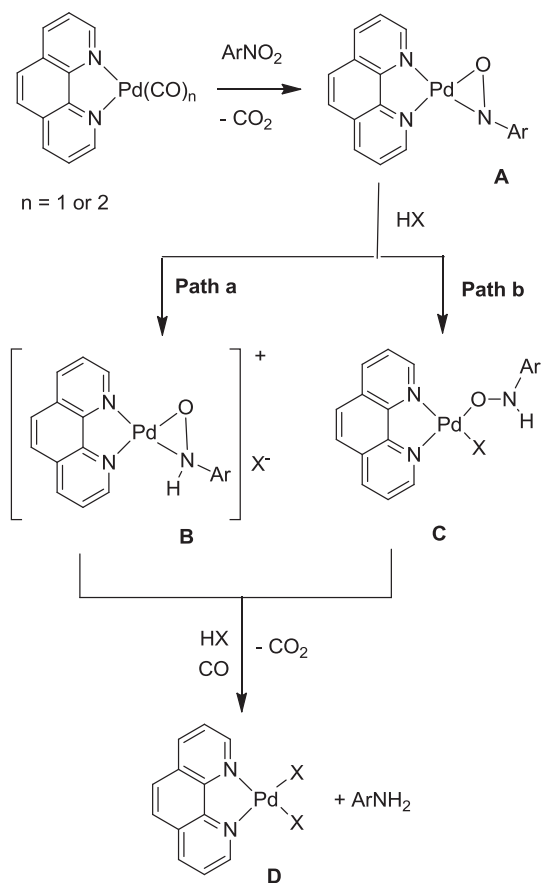
remains in the flask. If the reaction is performed in CDCl$_3$, the same stoichiometry is observed. The NMR spectrum of the solution after the addition of one or two equivalents of hydroxylamine is very similar, indicating that no intermediate products are formed and two equivalents of hydroxylamine are required to obtain the first observable complex. The solubility of **1** in CDCl$_3$ is so low that its signals are not observable by NMR. The only clearly observable signals are due to a complex (**2**) that contains a neocuproine ligand in a non-symmetric coordination environment and an equivalent amount of monodeprotonated hydroxylamine. Two signals in 2:1 ratio and a very broad one are always present, that can be ascribed to the formation of 3,5-dichlorophenylhydroxylammonium nitrate, by deprotonation of the first equivalent of hydroxylamine by the second one, exchanging with an unreacted neutral form in solution. The experiment was performed several times by adding even larger amounts of hydroxylamine. In all cases, the signals related to complex **2** discussed above were observable at the beginning of the reaction. The position of the broad peak and of those attributed to the hydroxylammonium nitrate shifts depending on the concentration of the hydroxylamine, in accord with a fast proton exchange with excess hydroxylamine.

The NMR spectrum of the main species in solution (**2**) is consistent with a hydroxylaminato complex, but the observed signals cannot discriminate between a structure of type **B** or **C** in Scheme 1.

Addition of benzene to the reaction solution a few minutes after the addition of two equivalents of hydroxylamine and concentration of the reaction mixture resulted in the precipitation of a solid that was immediately analyzed by mass spectroscopy (FAB$^+$). The only clearly observable group of peaks perfectly matches the mass and isotopic distribution of the [Pd(Neoc)(ONHC$_6$H$_3$Cl$_2$)]$^+$ fragment