Reaction of Arylhydroxylamines with [Pd(Neoc)(NO_3)$_2$] (Neoc = Neocuproine). Non-Innocent Behavior of the Nitrate Anion.

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Dedicated to Dr. Carlo Mealli on occasion of his 70th birthday.

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)($ONHC_6H_3Cl_2$)(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)($ON(3,5\text{-}C_6H_3Cl_2)NO$)][$NO_3$] (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.

Keywords: Palladium; Arylhydroxylamines; Phenanthroline; Nitrate; Nitroarenes

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 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

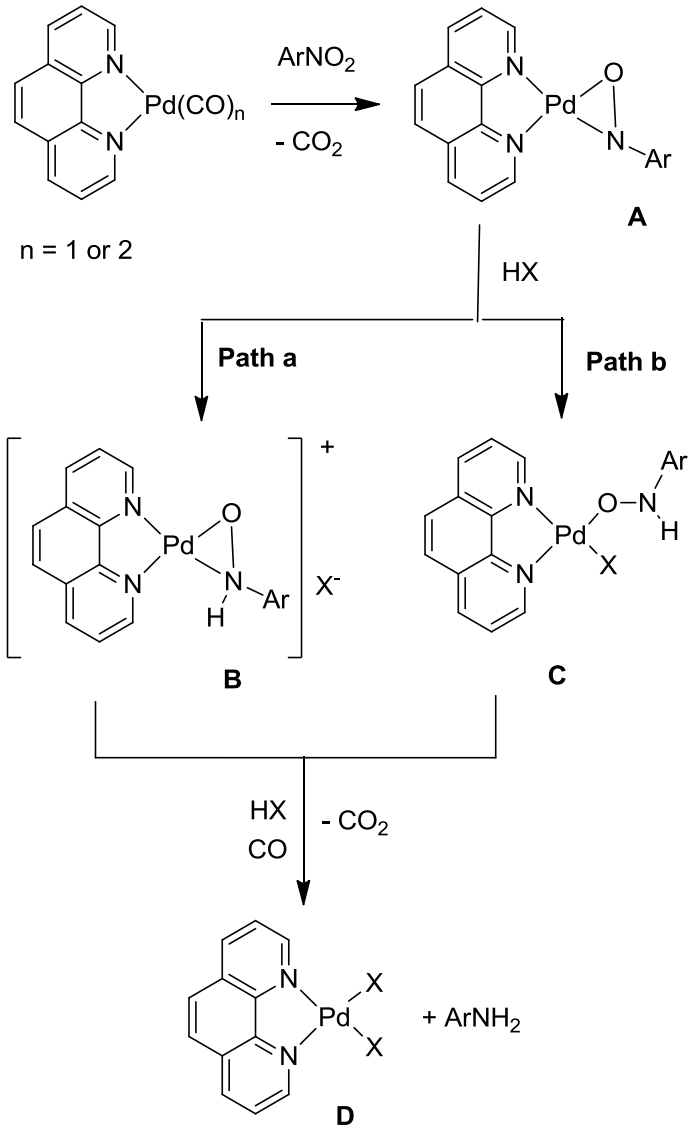
the corresponding nitrosoarene, which should remain bound to the metal, either in an η_2 complex [19] or as part of a metallacycle that also includes CO and/or CO_2 [8, 9, 20-24]. Although "on paper" it is easy to draw mechanisms that lead to the direct evolution of aryl isocyanates from the isolated 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 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.



Scheme 1

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_2Cl_2, but dissolves quickly upon addition of 3,5-$Cl_2C_6H_3NHOH$. At least two equivalents of hydroxylamine are required to complete the reaction, otherwise undissolved **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-dichlorophenylhydroxylamonium 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 signal 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 $[Pd(Neoc)(ONHC_6H_3Cl_2)]^+$ fragment (Figure S2). This observation strongly supports our proposal for the composition of **2**, but again does not allow a definitive conclusion of the structure since the nitrate ligand, if coordinated, is expected to be very labile and may be easily lost under the mass analysis conditions. Analysis of the same precipitate by IR spectroscopy, on the other hand, supports a structure of type **C** for **2**. The coordinated nature of the NO_3 ligand is suggested by the lack of IR absorption bands at 830-825 cm^{-1} typical of free nitrate ion [46, 47] and by the presence of strong bands at 807 and 792 cm^{-1}, a broad weak one at 993, and a medium one at 1270 cm^{-1} that can be attributed to a O-coordinated NO_3 group [44, 46, 47]. Complex **2** is thus [Pd(Neoc)(ONH(3,5-$C_6H_3Cl_2$))(NO_3)].

Unfortunately, we have been unable to obtain crystals of **2** suitable for X-ray diffraction analysis. This is partly due to the instability of **2** both in solution and in the solid state. Indeed, when a solution of **2** is left at RT for several hours, a yellow/orange precipitate invariably forms. In one case, from a $CDCl_3$ solution stored at -20 °C, some crystals were present which were suitable for X-ray diffraction

analysis. The characterized compound, **3**, is a N-aryl-N-nitrosohydroxylaminato complex, [Pd(Neoc)(ON(3,5-$C_6H_3Cl_2$)NO)][NO_3], in which a nitrosoarene moiety is coupled with a nitrogen oxide molecule (Figure 1). A more detailed description of the solid state structure of this compound is given in the following paragraph.

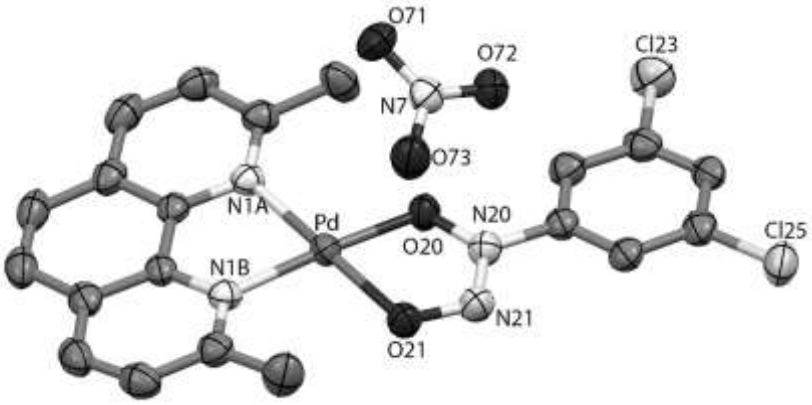


Figure 1. ORTEP plot of [Pd(Neoc)(ON(3,5-$C_6H_3Cl_2$)NO)][NO_3] in **3**. Solvent molecules of $CHCl_3$ and H atoms are omitted for the sake of clarity. Ellipsoids are drawn at 50% probability level. The $(NO_3)^-$ anion is not coordinated to the metal complex.

Complex **3**, as well as the analogous palladium phenanthroline complexes, have not previously been reported in the literature but several complexes are known featuring a -ON(Ar)NO- ligand. In most cases, they were obtained by reaction of a nitrosoarene complex with NO (for an example of a palladium complex see [48]), although in some cases the preformed anionic ligand, a stable organic molecule, was employed (for an example of a palladium complex see [49]).

When the reaction was conducted for a prolonged time (4 h) in CH_2Cl_2, a sample of the bulk of the solid precipitated by the addition of benzene, not a single crystal, was subjected to mass analysis (FAB^+). Only the peaks due to the [Pd(Neoc)(ON(3,5-$C_6H_3Cl_2$)NO)]$^+$ ion could be identified clearly, supporting the view that the analyzed single crystal is not a minor component of the solid, but a major one.

When the reaction between **1** and 3,5-$Cl_2C_6H_3NHOH$ was performed in the presence of one equivalent of triethylamine, in $CDCl_3$, just a 10% molar excess of hydroxylamine with respect to palladium was sufficient to complete the reaction. The ^{1}H NMR spectrum of the solution showed the signals due to complex **2** (Figure S1). No broad peaks were detected and just very small peaks related to non-coordinated hydroxylamine were present. In addition, two peaks related to Et_3N were detected (quartet at 3.16 and triplet at 1.35 ppm) whose chemical shift are typical of triethylammonium salts in $CDCl_3$ (quartet at around 3.1 and triplet at around 1.3 ppm, free Et_3N: 2.53 (q), 1.03 (t) ppm). This result confirms that the second equivalent of hydroxylamine required to complete the reaction when no other reagent is added is simply acting as a base and is not necessary if another, stronger, base is present.

Crystalline **3** is insoluble in $CDCl_3$, but soluble in D_2O and a clean ^{1}H NMR spectrum could be obtained by dissolving some single crystals in the latter solvent (Figure S3). The spectrum is in accord with the structure determined by X-ray diffraction.

The origin of the NO moiety in **3** is not obvious at this stage. The nitrate anion is clearly a candidate, but a NO group may also derive from a decomposition of hydroxylamine. Loss of the -NO_2 group from nitroarenes is known to occur in some cases [50] and NO loss from nitroso compounds is also known, albeit it usually requires irradiation [51]. A piece of information on this point was obtained fortuitously when a CH_2Cl_2 solution obtained by reacting **1** with two equivalents of 3,5-$Cl_2C_6H_3NHOH$ was stored at -20 °C. A few crystals of a new complex, **4**, formed. Single crystal X-ray analysis of **4** showed it to be an unusual nitro-nitrato complex (Figure 2).

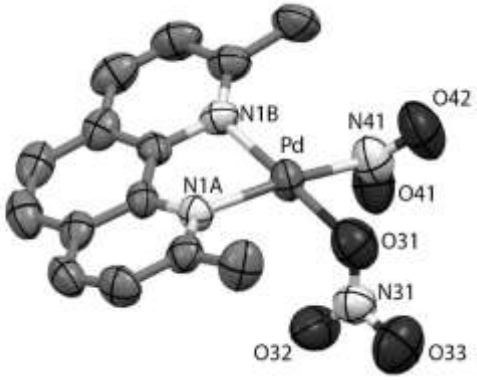
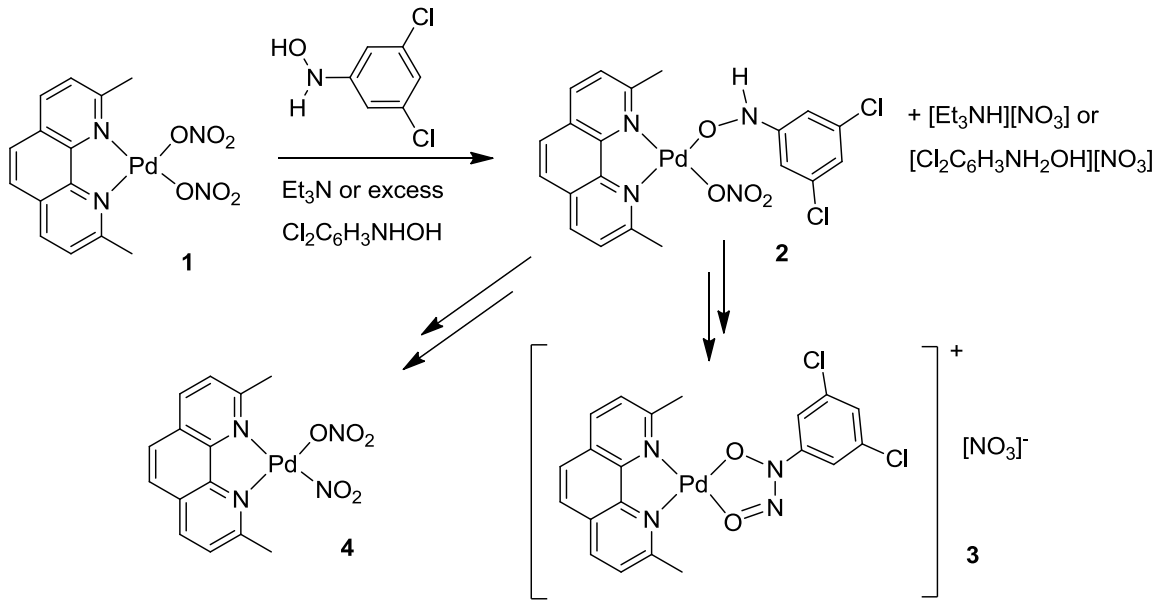


Figure 2 ORTEP plot of [Pd(Neoc)(NO_3)(NO_2)] (**4**). Solvent molecules of CH_2Cl_2 and H atoms are omitted. Ellipsoids are drawn at 50% probability level. Here, the $(NO_3)^-$ is directly coordinated to the metal.

The structure of **4** is described in more details in the following paragraph. What is important to evidence here is that the isolation of this compound leads strong support to the idea that the NO moiety in **3** derives from the reduction of a nitrate ion. Such scenario also indirectly supports the conclusion drawn from the IR spectra that the nitrate ion is coordinated in **2**. Indeed, coordinated nitrate should be a stronger oxidant than the free anion and the *cis* disposition of the hydroxylaminato and nitrate anions forced by the chelating ligand is ideally suited to promote an interaction between the two. Scheme 2 summarizes the results obtained.



Scheme 2

2.2 Crystal structure of [Pd(Neoc)(ON(3,5-$C_6H_3Cl_2$)NO)][NO_3] (3) and [Pd(Neoc)(NO_3)(NO_2)] (4).

Both compounds feature a square planar Pd(II) metal ion and a distorted neocuproine ligand. The two Pd-N bond length are very close, although no molecular (nor of course any crystal) symmetry exists. In Figures 1 and 2, the molecular geometries of the two complexes are shown. For **3**, the nearest $(NO_3)^-$ non-coordinated counterion is also shown, whereas clathrated solvent molecules are omitted.

In **3**, the similarity of the coordination by the two oxygens of the N-aryl-N-nitrosohydroxylaminato moiety to Pd, makes also the neocuproine ligand more symmetrically attached to Pd. As a matter of facts, Pd1-O20 and Pd1-O21 distances are almost identical (1.991(3) and 2.003(3) Å, respectively), and so are Pd1-N1A and Pd1-N1B (2.041(3) and 2.031(3) Å, respectively). The ONN(Ar)O system is very delocalized, in fact N20-O20 is just slightly longer than N(21)-O(21) (1.336(4) Å and 1.300(4) Å, respectively) and N20-N21 is 1.273(5) Å, which would be a rather short distance for a N-N single bond. This high delocalization justifies the rather similar Pd-O bonds. On the other hand, the N(20)-Ar distance is quite long (1.439(5) Å), indicating a clearly localized C-N single bond.

In **4**, the coordination of nitro and nitrato ligands is quite different. Pd1-N41 (2.016(7) Å) is in perfect agreement with the average distance in -NO_2 coordinated Pd complexes (2.018(2) Å), as found in the Cambridge crystallographic database [52]. The coordination to the nitrate oxygen is instead shorter than the average from the Cambridge crystallographic database (2.030(7) vs. 2.080(5) Å).

The difference between the two bonds produces a slight asymmetry also in the coordination of neocuproine. In fact, Pd1-N1A, which is *trans* to the nitro-ligand, is slightly longer than Pd1-N1B (2.064(5) vs. 2.029(6) Å), which is *trans* to the nitrate ligand.

The steric effect of the methyl groups is quite evident in the angle between the average plane of the neocuproine ligand and the square plane defined by the Pd and the four atoms attached to it: 15(1)° in **3** and 28(1)° in **4**. Moreover, in **4**, the steric hindrance between NO_2 and NO_3 groups, makes their

planes almost vertical with respect to the coordination plane of the Pd atom (69(1)° and 80(1)°, respectively).

Despite not directly coordinated to the Pd atom, the nitrate group in **3** is packed close to the complex, forming weak interactions with the N-aryl-N-nitrosohydroxylaminato group. Additional interactions of the nitrate are formed with the $CHCl_3$ molecules. The complex, instead, features a weak antiparallel stacking with another complex molecule, so that the motif $(NO_3)^-$--- ONN(Ph)O--- -ON(Ph)NO---$(NO_3)^-$ is recognizable. In **4**, almost all intermolecular interactions are mediated by the co-crystallized CH_2Cl_2, with the only exception of some weak C-H---O-NO_2 interactions.

3. Conclusions

Our study was aimed at isolating and characterizing a palladium arylhydroxylaminato complex with a phenanthroline-type ligand. The results were only partly successful because the desired complex was apparently obtained indeed, but was not stable enough to be isolated in a pure form and characterized by X-ray diffraction. On the other hand, two of the decomposition products could be identified clearly and give a plausible picture of what is occurring in solution. Retrospectively, the choice of nitrate as a counterion for palladium was not the right one. It had been chosen because it was considered to be the most labile anion still able to allow the isolation of a complex of type $[Pd(Neoc)(X)_2]$ instead of $[Pd(Neoc)_2][X]_2$, the latter type being invariably obtained with non-coordinating anions like BF_4^- or PF_6^-. However, its oxidizing power was underestimated and caused an easy decomposition of the complex. Future studies will focus on the use of non-oxidizing counteranions.

4. Experimental section

4.1. Methods and materials

All the syntheses were performed under a dinitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 and Et_3N were distilled over CaH_2 and stored under a dinitrogen atmosphere. THF and benzene were distilled over sodium/benzophenone ketyl and stored under a dinitrogen atmosphere. $[Pd(Neoc)(NO_3)_2]$ was synthesized as previously reported by us [45]. $CDCl_3$ was passed over basic alumina, degassed and kept over activated 4 Å molecular sieves under an inert atmosphere (N_2). All the other reagents were purchased form Sigma Aldrich and used without further purification. All glassware and magnetic stirring bars were kept in an oven at 125 °C overnight and let to cool under vacuum before use. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 300 or on a Bruker Avance DRX 400. Chemical shifts are reported in ppm relative to TMS. Elemental analyses were performed on a Perkin Elmer 2400 CHN elemental analyzer. IR spectra were registered on a Varian Scimitar FTS-1000.

4.2. Synthesis of *N*-(3,5-dichlorophenyl)hydroxylamine

The synthesis was performed by a modification of a previously reported method [53]. 3,5-Dichloronitrobenzene (1.011 g, 5.26 mmol) was dissolved in THF (50 mL) in a three-neck flask. 10%

Pd/C (0.110 g) was added under nitrogen while stirring. After cooling to 0 °C with an ice bath, 35 wt.% hydrazine in water (1.2 mL, 13.2 mmol) was added and the mixture stirred for 1h. The end of the reaction was check by TLC (EtOAc/Hexanes = 3:7). The reaction mixture was filtered through Celite and the volatiles removed by rotary evaporation to afford a yellow solid. The product was dissolved in CH_2Cl_2 and dried over Na_2SO_4. Filtration and evaporation of the solvent afforded the hydroxylamine in 90% yield (0.846 g, 4.75 mmol). The product was stored under nitrogen at -20°C to avoid decomposition. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (s, 1H), 6.88 (s, 2H), 6.78 (br s, 1H, OH), 5.23 ppm (br s, 1H, NH). The NMR spectrum was in accordance with that previously reported [54]. Elem. Anal calcd for $C_6H_5Cl_2NO$: C 40.48, H 2.83, N 7.87; found: C 40.69, H 2.71, N 8.05.

4.3. Reaction of [Pd(Neoc)(NO$_3$)$_2$] (1) with variable amounts of *N*-(3,5-dichlorophenyl)hydroxylamine in CDCl$_3$.

In an NMR tube, **1** (5.0 mg,) was suspended in $CDCl_3$ (1.5 mL) under nitrogen. A $CDCl_3$ (25 μL) solution of *N*-(3,5-dichlorophenyl)hydroxylamine (1 equivalent) was added. The initial complex **1** did not dissolve completely. A second equivalent of hydroxylamine was added and the tube thoroughly shaken. Complex **1** dissolved almost completely. Addition of 2 more equivalents of hydroxylamine did not lead to any appreciable change in the aspect of the reaction mixture. ^{1}H NMR spectra were recorded after every addition. ^{1}H NMR after addition of 1 equiv. of $Cl_2C_6H_3NHOH$ (300 MHz, $CDCl_3$) δ 11.47 (br s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H, CH $_{Neoc}$), 8.38 (d, *J* = 8.4 Hz, 1H, CH $_{Neoc}$), 7.89 (d, *J* = 9.1 Hz, 1H, CH $_{Neoc}$), 7.85 (d, *J* = 9.1 Hz, 1H, CH $_{Neoc}$), 7.78 (d, *J* = 8.3 Hz, 1H, CH $_{Neoc}$), 7.73 (s, 2H, CH $_{Ar}$), 7.65 (d, *J* = 8.4 Hz, 1H, CH $_{Neoc}$), 7.29 (s, 1H, CH $_{Ar}$), 2.81 (s, 3H, CH$_{3\ Neoc}$), 2.68 (s, 3H, CH$_{3\ Neoc}$). Additional signals due to protonated *N*-(3,5-dichlorophenyl)hydroxylamine possibly in exchange with the free one: 6.92 (s, 2H), 6.88 ppm (s, 1H) and a broad signal shifting from 9.1 to 7.4 ppm depending on the hydroxylamine concentration were present. From one reaction performed with 2 equivalents of hydroxylamine in $CDCl_3$ and stored at -20°C, single crystals of **3** suitable for X-ray diffraction were obtained. The crystals were insoluble in $CDCl_3$, but soluble in D_2O and a clean ^{1}H NMR spectrum of **3** could be obtained this way: ^{1}H NMR (300 MHz, D_2O) δ 8.45 (d, *J* = 9.0 Hz, 1H, CH $_{Neoc}$), 8.34 (d, *J* = 8.1 Hz, 1H, CH $_{Neoc}$), 7.79 – 7.66 (m, 3H, CH $_{Ar}$ and CH $_{Neoc}$), 7.58 (d, *J* = 8.1 Hz, 1H, CH $_{Neoc}$), 7.52 (d, *J* = 9.0 Hz, 1H, CH $_{Neoc}$), 7.43 (s, 2H, CH $_{Ar}$), 2.79 (s, 3H, CH$_{3\ Neoc}$), 2.70 ppm (s, 3H, CH$_{3\ Neoc}$).

4.4. Reaction of [Pd(Neoc)(NO$_3$)$_2$] (1) with 2 eq. of *N*-(3,5-dichlorophenyl)hydroxylamine in CH$_2$Cl$_2$.

In an oven-dried Schlenk tube, **1** (21.8 mg, 0.05 mmol) was suspended in CH_2Cl_2 (8 mL) and *N*-(3,5-dichlorophenyl)hydroxylamine (18.6 mg, 0.10 mmol) was added while stirring. The initial complex **1** dissolves almost immediately. Stirring was continued for 15 minutes after which only a very little amount of insoluble solid was present. The mixture was filtered by cannula technique. Part of the solution was separated and cooled at -20 °C. Benzene (10 mL) was added to the remaining part and the reaction concentrated under vacuum until a yellow solid precipitated. The solid was collected by filtration on a sintered frit under nitrogen, washed with benzene (2 mL) and immediately analyzed by FAB MS (glycerol matrix) and ^{1}H NMR. MS (FAB): *m/z* 492 (calcd. for $[Pd(Neoc)(ONHC_6H_3Cl_2)]^+$ = 492. See the supporting information for a comparison between the experimental isotopic pattern and the calculated one). Single crystals of [Pd(Neoc)(NO_3)(NO_2)] (**4**) were obtained from the part of the solution stored at -20°C.

An analogous reaction was performed stirring the initial CH_2Cl_2 reaction mixture for 4 h. After addition of benzene (8 mL) and concentration of the reaction mixture, an orange/yellow solid was obtained that was dried under vacuum for several hours. MS (FAB): *m/z* 521 (calcd for $[Pd(Neoc)(ON(3,5\text{-}C_6H_3Cl_2)NO)]^+$ = 521. See the supporting information for a comparison between the experimental isotopic pattern and the calculated one.).

4.5. Reaction of [Pd(Neoc)(NO_3)$_2$] (1) with *N*-(3,5-dichlorophenyl)hydroxylamine using E_3N as external base.

In an oven-dried Schlenk tube, **1** (20.6 mg, 4.7×10^{-2} mmol) was suspended in $CDCl_3$ (8 mL) and *N*-(3,5-dichlorophenyl)hydroxylamine (9.1 mg, 5.1×10^{-2} mmol) was added while stirring. The initial complex **1** is only partially dissolved even after 5 minutes. The initial complex dissolves completely only after addition of triethylamine (7.5 μL, 5.4×10^{-2} mmol). The mixture was immediately analyzed by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (br s, 1H), 8.49 (d, *J* = 8.3 Hz, 1H, CH_{Neoc}), 8.37 (d, *J* = 8.2 Hz, 1H, CH_{Neoc}), 7.91 (d, *J* = 8.6 Hz, 1H, CH_{Neoc}), 7.85 (d, *J* = 8.6 Hz, 1H, CH_{Neoc}), 7.80 (s, 2H, CH_{Ar}), 7.76 (d, *J* = 8.2 Hz, 1H, CH_{Neoc}), 7.63 (d, *J* = 8.3 Hz, 1H, CH_{Neoc}), 7.29 (s, 1H, CH_{Ar}), 2.81 (s, 3H,$CH_{3\ Neoc}$), 2.72 (s, 3H, $CH_{3\ Neoc}$). Additional signals related to species derived from *N*-(3,5-dichlorophenyl)hydroxylamine: 6.80 (s), 6.75 ppm (s). Triethylammonium salt: 3.25 – 3.11 (m, 6H), 1.35 ppm (t, *J* = 7.2 Hz, 9H).

4.6. Single crystal X-ray diffraction.

For both crystal species, the samples were mounted in air at ambient conditions and measured at ambient temperature. All measurements were made on a *Bruker-APEXII* area-detector diffractometer [55] using graphite monochromated Mo *K*α radiation (λ = 0.71073 Å). The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of strongest reflections. The frames were collected using ω scans, with 40 seconds (for **3**) and 60 seconds (for **3**) exposure time per frame, a rotation angle of 0.5° per frame, a crystal-detector distance of 50.0 mm.

Data reduction was performed using the *APEX2* program. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SADABS [56].

The structure was solved by direct methods using *SHELXT* [57], which revealed the positions of all non-hydrogen atoms of the title compound. All non-hydrogen atoms were refined anisotropically (including solvent molecules). All H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 Ueq of its parent atom.

Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the *SHELXL-2014/7* [58] program.

Data collection and refinement parameters are given in Tables S1 and S5. Details of the refined models and in Tables S2-S4 and S6-S8.

CCDC 1540684 and 1540685 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

5. Supplementary material

Copies of ^{1}H NMR and mass spectra, crystallographic material for compounds **3** and **4.**

6. Acknowledgements

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Graphical Abstract