

Interplay between Nitrones and (Nitrile)Pd^{II} Complexes: Cycloaddition vs. Complexation Followed by Cyclopalladation and Deoxygenation Reactions

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The reaction between the nitron *p*-MeC₆H₄CH=N(Me)O and *trans*-[PdCl₂(RCN)₂] (R = Ph, Me) in the corresponding RCN (or of the nitron in neat RCN in the presence of PdCl₂) proceeds at 45 °C (R = Ph) or reflux (R = Me) for 1 d and allows the isolation of the Δ⁴-1,2,4-oxadiazoline complexes [PdCl₂{N^a=C(R)ON(Me)C^bH(C₆H₄Me-*p*)}₂(N^a-C^b)] (R = Ph **1**; R = Me **2**) in ca. 50 and ca. 15 % yields, respectively. The reaction time can be drastically reduced by focused microwave irradiation of the reaction mixture. In CH₂Cl₂ or acetone, this reaction proceeds in another direction to achieve the unstable nitron complex [PdCl₂{ON(Me)=CH(C₆H₄Me-*p*)}₂] (**3**), which was characterized by electrospray mass spec-

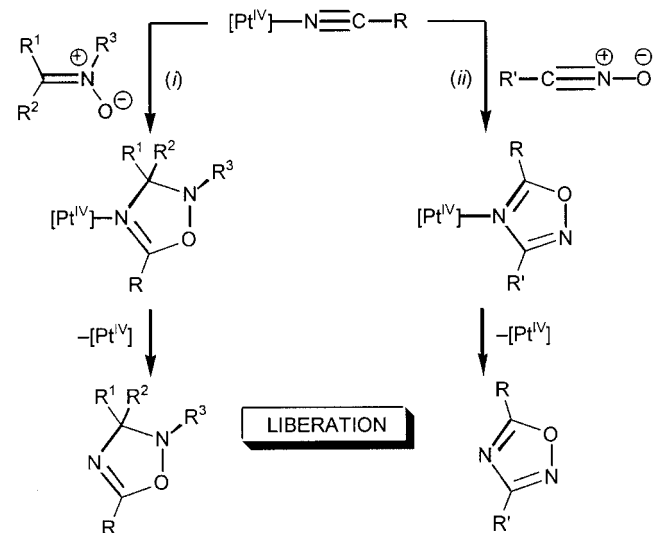
troscopy, IR and ¹H NMR spectroscopy. Complex **3** is the first representative of (nitron)Pd^{II} compounds and is the key intermediate in at least two further reactions, i.e. cyclopalladation to give the dimeric complex [Pd₂(μ-Cl)₂{ON(Me)=C(H)C₆H₃Me-*p*}₂] (**5**; 30 % isolated yield) and deoxygenation of the nitron to furnish the imine compound [PdCl₂{N(Me)=CH(C₆H₄Me-*p*)}₂] (**4**). The palladium complexes **1**, **2**, **4** and **5** were characterized by C, H, and N analyses, FAB-MS, IR, ¹H and ¹³C{¹H} spectroscopy, while **4** and **5** additionally by X-ray crystallography.

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Introduction

In organic chemistry, 1,3-dipolar cycloadditions are reactions of paramount importance for the synthesis of a great variety of heterocycles.^[1–5] One of the most promising sub-directions of research in this area includes metal control of the interplay between various dipolarophiles and dipoles. Indeed, metal-mediated cycloadditions have been the object of extensive investigations in the past decade and substantial progress has been achieved in both stoichiometric and catalytic approaches.^[5–8] In the overwhelming majority of these works, *alkenes* have been employed as dipolarophiles, whereas application of *organonitriles* for these purposes was investigated to an incomparably lesser degree.^[6,7] Recently we found that significant activation of nitriles—even typically unreactive ones bearing an electron-donor R group in RCN—toward cycloadditions of both allyl anion (i.e., nitrones,^[8–11] route *i* in Scheme 1) and propargyl/allenyl anion

type (i.e., nitrile oxide,^[12,13] route *ii*) dipoles^[11,2] can be reached by their ligation to a Pt^{IV} center, while Pt^{II} displays little effect^[10] on the reaction. Subsequent liberation of the ligands allowed the metal-mediated synthesis of these two classes of heterocycles.



Scheme 1.

As a continuation of our project on reactions of metal-activated nitriles in general^[6,14] and 1,3-cycloadditions^[8–13] in particular, we have chosen (nitrile)Pd^{II} complexes as di-

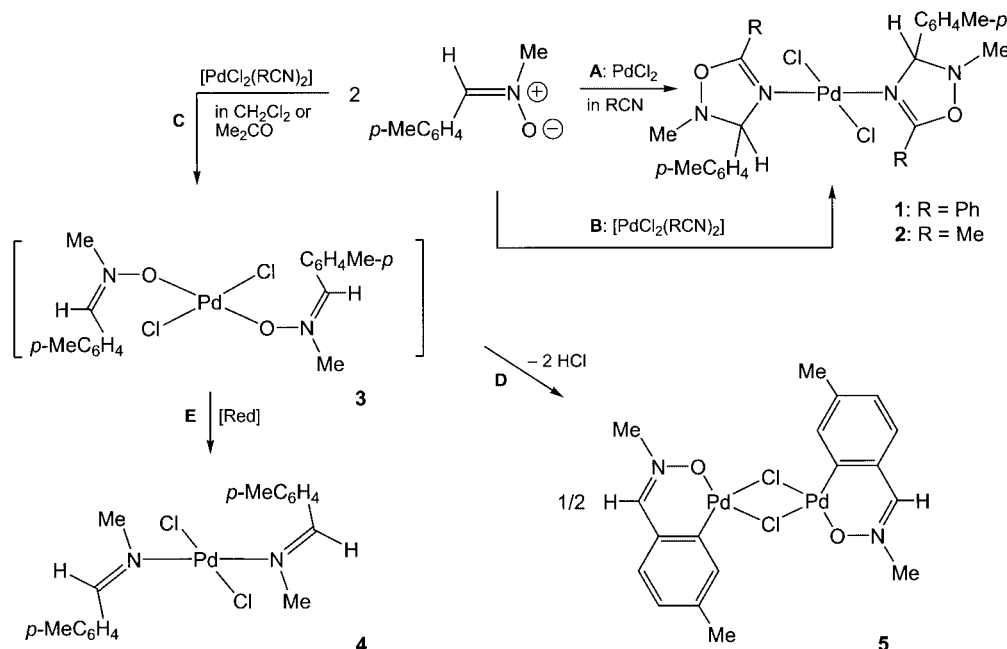
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Scheme 2.

polarophiles and observed a palladium-mediated [2 + 3] cycloaddition of a nitron to achieve (Δ^4 -1,2,4-oxadiazoline)-Pd^{II} complexes. A recent brief report^[15] on the occurrence of this type of reaction for the benzonitrile complex [PdCl₂(PhCN)₂], including an indication that the analogous acetonitrile compound is unreactive, prompted us to display our own results in this field. In contrast to that work, we have observed not only that the [2 + 3] cycloaddition proceeds for [PdCl₂(MeCN)₂] but also that other types of reactions, i.e. cyclopalladation and nitron deoxygenation, take place in these systems. The occurrence of the latter two processes, which were not previously observed in the chemistry of nitrones, explains the lack of selectivity of the cycloaddition and provides further insight into understanding the effect of the metal center upon the cycloaddition.

Results and Discussions

We chose to study the reaction of palladium(II) complexes *trans*-[PdCl₂(RCN)₂], bearing nitriles with acceptor (R = Ph) and donor (R = Me) substituents, with a stable nitron, *p*-MeC₆H₄CH=N(Me)O, as the dipole/ligand.

Palladium(II)-Mediated 1,3-Dipolar Cycloaddition

The reaction between the nitron *p*-MeC₆H₄CH=N(Me)O and PhCN mediated by a Pd^{II} center was performed by two similar, although technically distinct, routes (Scheme 2, routes A and B).

In the first route (A), both PdCl₂ and the nitron *p*-MeC₆H₄CH=N(Me)O were reacted in a suspension of neat PhCN, while in the second route (B) the nitrile complex *trans*-[PdCl₂(PhCN)₂],^[16] dissolved in the corresponding ni-

trile, was treated with the nitron. In both routes, the reaction proceeds at 45 °C for 1 d (or for 4 h under 20 W microwave irradiation) and the isolated yield of the Δ^4 -1,2,4-oxadiazoline complex [PdCl₂{N^a=C(Ph)ON(Me)C^bH(C₆H₄-Me-*p*)}₂(N^a-C^b)] (1), prepared by the two methods, is almost the same (ca. 50%) irrespective of whether conventional or microwave conditions are applied.

The reaction of PdCl₂ with neat PhCN is well known and it constitutes a method for the preparation of *trans*-[PdCl₂(PhCN)₂].^[16] Hence, it is not surprising that the reaction rates and the isolated yields are similar for both routes, because the first route conceivably includes the formation of [PdCl₂(PhCN)₂] (upon dissolution of PdCl₂ in PhCN) followed by the cycloaddition of the nitron. Despite the similarity of the synthetic approaches A and B, the obvious advantage of the former method is that it allows us to obtain complex 1 starting directly from PdCl₂ and omitting the unnecessary step of the isolation of *trans*-[PdCl₂(PhCN)₂].

The complex 1 gave satisfactory microanalysis for the PhCN solvate and the expected fragmentation/isotopic pattern in FAB-MS⁺ ([M - Cl]⁺ and [M - 2 HCl]⁺). In the IR spectrum, the complex exhibits a strong band at 1649 cm⁻¹ from ν (C=N) of the heterocycle and 2231 cm⁻¹ from ν (C≡N) of the solvate. In the ¹H NMR spectrum, the Δ^4 -1,2,4-oxadiazoline ring displays signals in the aromatic range from 8.62 to 7.32 ppm, two Me groups appear at 2.90 and 2.43, and the CH signal emerges at δ = 5.82 ppm. Excess of Ph's from the solvated PhCN were detected in the spectrum by integration. All our data agree well with the previously reported formulation.^[15] In addition, we performed an X-ray analysis of 1 and it is indicated that the *R,R*- and *S,S*- Δ^4 -1,2,4-oxadiazoline ligands are in the mutu-

ally *trans*-positions (see Figure 1 and deposited data). Unfortunately, the rather poor quality of crystals precluded a detailed comparison of the geometrical parameters.

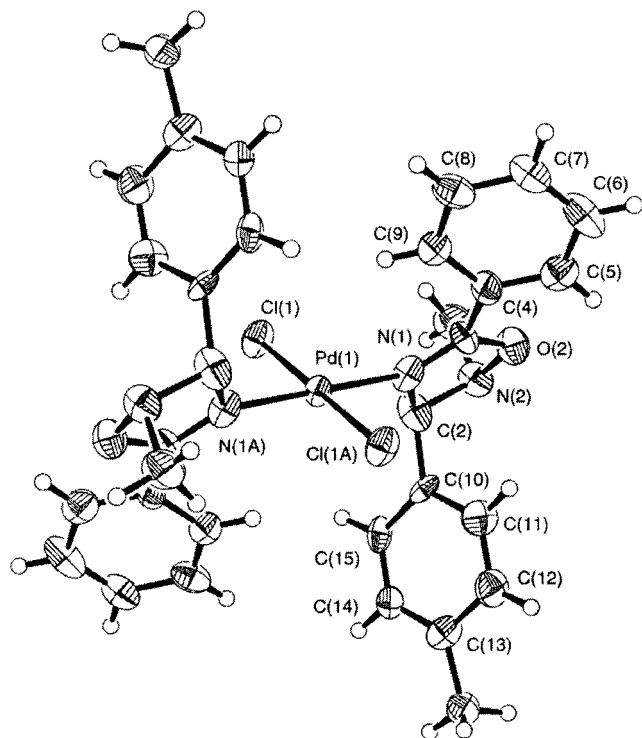


Figure 1. ORTEP view of **1**.

Previously, it has been reported that the acetonitrile complex $[\text{PdCl}_2(\text{MeCN})_2]$ is unreactive toward the nitron $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ even under relatively harsh conditions (80 °C, 1 week).^[15] In contrast to that report, in our hands, an interplay between the nitron $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ and $[\text{PdCl}_2(\text{MeCN})_2]$ (or with PdCl_2) in MeCN (Scheme 2, A and B) upon reflux for 1 d (or, 20 min at ca. 80 °C under 70 W microwave irradiation) results in the formation of a broad mixture of products, where the complex **2**, derived from the 1,3-dipolar cycloaddition is formed in 10–15% ^1H NMR yield [integration is based on the $\text{CH}(\text{R})$ proton of the ring which usually emerges in a very specific region from 5.0 to 6.0 ppm]. The complex $[\text{PdCl}_2\{\text{N}^a=\text{C}(\text{Me})\text{ON}(\text{Me})\text{C}^b\text{H}(\text{C}_6\text{H}_4\text{Me}-p)\}_2\text{-}(\text{N}^a\text{-C}^b)]$ (**2**) was isolated as a solid and characterized as the bis-hydrate (see Exp. Sect.). Microwave irradiation of the reaction mixture did not improve the selectivity of the cycloaddition but allowed the dramatic reduction of the reaction time.

Coordination of the Nitron and Subsequent Reactions

In general, dissociation of RCN from (nitrile) Pd^{II} complexes in non-nitrile solutions (vs. nitrile ones), similar to that described for weak electrolytes by the Ostwald dilution law, increases and consequently the amount of ligated RCN decreases thus favouring the substitution via the expected dissociative mechanism. Thus, to increase the fraction of

reactions other than the cycloaddition and to understand the lack of selectivity, indicated in the previous section, we studied the reaction between $[\text{PdCl}_2(\text{RCN})_2]$ complexes and the nitron $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ in dichloromethane and acetone. Indeed, in these experiments we did not detect complexes **1** and **2** but the complex $[\text{PdCl}_2\{\text{ON}(\text{Me})=\text{CH}(\text{C}_6\text{H}_4\text{Me}-p)\}_2]$ (**3**) (Scheme 2, route C), which originates from the substitution, was isolated. Although **3** is unstable even in the solid state and undergoes further reactions in solutions (see later) we succeeded to characterize this product by electrospray mass spectrometry ($[\text{M} - \text{HCl}]^+$ and $[\text{M} - 2\text{HCl}]^+$ ions were observed). In the IR spectrum of **3**, the $\nu(\text{C}=\text{N})$ stretching vibration is shifted to a higher frequency (by, 14 cm^{-1}), while the $\nu(\text{N}-\text{O})$ stretch is shifted to a lower frequency (by 10 cm^{-1}) vs. those signals in the free nitron and these observations favour *O*-coordination of the nitron to a Pd^{II} center.

Complexes with *O*-bound nitrones as ligands are known although scarce. These species can be formed (i) in the direct reaction of a nitron and a metal complex at various metal centers such as *hard* (U^{VI} ,^[17] Zn^{II} ,^[18,19] Sn^{IV} ,^[20] Ti^{IV} ,^[15,21] Zr^{IV} ,^[15] *soft* (Au^{I} ,^[22] Au^{III} ,^[22] Ag^{I} ,^[19] and *borderline* (Ni^{II} ,^[23] Cu^{II} , Mn^{II} , Co^{II} , Fe^{II} , Fe^{III} ,^[24,25] and Ru^{II} - and Os^{II} ,^[26] porphyrines) Lewis acids and (ii) in a metal-mediated process, e.g. by reaction of a carbene ligand with nitrosoarenes at an Fe^{II} center^[27] or by addition of 2-methyl-2-nitrosopropane to coordinated ethylene^[28] at a Pt^{II} center. To the best of our knowledge, the complex **3** is the first representative of a (nitron) Pd^{II} compound.

We believe that the nitron complex **3** can be the key intermediate in at least two further reactions, which are observed in this work, i.e. cyclopalladation to give the dimeric complex $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{ON}(\text{Me})=\text{C}(\text{H})\text{C}_6\text{H}_3\text{Me}-p\}_2]$ **5** (Scheme 2, route D) and deoxygenation of the nitron to furnish the imine compound $[\text{PdCl}_2\{\text{N}(\text{Me})=\text{CH}(\text{C}_6\text{H}_4\text{Me}-p)\}_2]$ **4** (Scheme 2, route E). Thus, **5** is released as crystals (yield is 30%) when the reaction mixture is kept in CH_2Cl_2 for 3 d at room temperature (Figure 2).

The dimer **5** was characterized by X-ray crystallography. Both palladium atoms form a square-planar arrangement with two mutually *trans* cyclometalated nitrones. The deviation of the metallacycle planes $\text{Pd}(1)\text{C}(1)\text{C}(7)\text{C}(8)\text{N}(1)\text{O}(1)$ from the $\text{Pd}(1)\text{Cl}(1)\text{Pd}(1\text{A})\text{Cl}(1\text{A})$ plane is 22.36°. The bond lengths $\text{Pd}-\text{Cl}$ (*trans* to O) [2.3234(6) Å] and $\text{Pd}-\text{Cl}$ (*trans* to C) [2.4712(6) Å] are normal and agree well with other palladium(II) halogen-bridged complexes.^[29] The difference in the $\text{Pd}-\text{Cl}$ bond lengths *trans* to O or *trans* to C are due to a strong ground state *trans*-influence of C-bonded ligands.^[30] The bond length $\text{C}(8)-\text{N}(1)$ [1.289(3) Å] is a double one^[31] and the bond length $\text{N}(1)-\text{O}(1)$ [1.331(2) Å] has a value that falls in the range of typical N–O bond lengths in *N*-oxides.^[31]

The data on stability of nitron metal complexes are quite limited in the literature and the only relevant information so far reported is for the iron complexes $[\text{Cp}(\text{CO})_2\text{-Fe}\{\text{ON}(\text{Ar})=\text{CH}(\text{Ar}')\}]^+$ which are light- and moisture-sensitive and decompose to the imine $\text{ArN}=\text{CH}(\text{Ar}')$ (by *deoxygenation*; the reducing agent was not verified^[27]) and

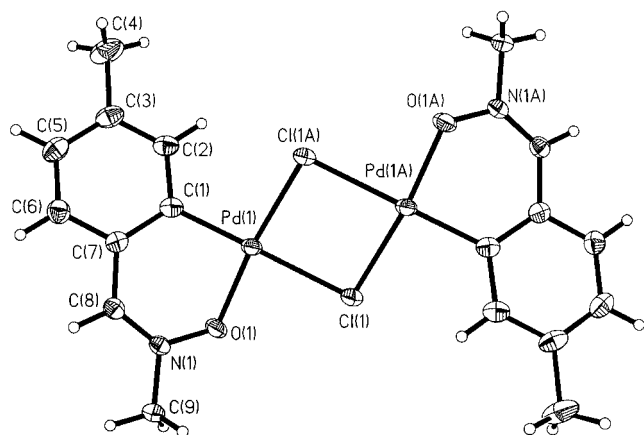


Figure 2. Thermal ellipsoid view of complex **4** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths [Å] and angles [°]: Pd(1)–N(1) 2.024(5), Pd(1)–Cl(1) 2.3058(16), N(1)–C(1) 1.250(8), N(1)–C(9) 1.469(8), C(1)–C(2) 1.473(10), N(1)–Pd(1)–Cl(1) 90.53(15), Pd(1)–N(1)–C(1) 126.7(5), Pd(1)–N(1)–C(9) 113.3(4), N(1)–C(1)–C(2) 126.8(6).

to aldehyde $\text{O}=\text{CH}(\text{Ar}')$ (by hydration) along with some unidentified iron-containing products.^[27] In accord with this report, we isolated (by mechanical separation of crystals obtained from evaporation of a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution of the residue of the reaction mixture PdCl_2 -*p*- $\text{MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ - PhCN) the aldimine compound $[\text{PdCl}_2\{\text{N}(\text{Me})=\text{CH}(\text{C}_6\text{H}_4\text{Me-}p)\}]_2$ (**4**) (Scheme 2, route E; Figure 3) which was characterized by X-ray diffraction study. In complex **4**, the palladium atom is in a square-planar arrangement and two aldimine ligands are mutually *trans*. The value of the C(1)–N(1) [1.250(8) Å] bond length is in the typical double bond range^[31] and the Pd–Cl [2.3057(16) Å] bonds are normal.^[31]

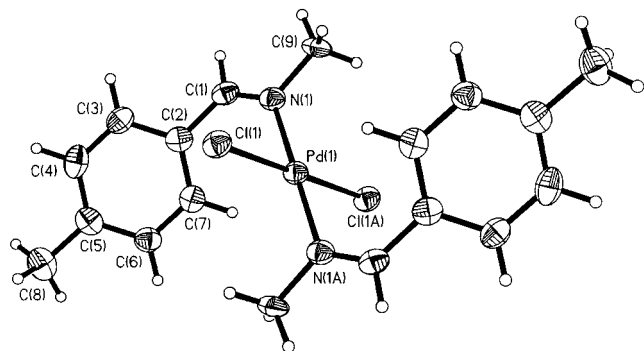


Figure 3. Thermal ellipsoid view of complex **5** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 1.973(4), Pd(1)–O(1) 1.996(3), Pd(1)–Cl(1) 2.4696(12), N(1)–O(1) 1.333(4), C(1)–Pd(1)–O(1) 92.21(15), C(1)–Pd(1)–Cl(1A) 94.65(13), O(1)–Pd(1)–Cl(1) 87.82(8), Pd(1)–Cl(1)–Pd(1A) 94.73(4).

A possible rationale for the formation of **4** is deoxygenation of the parent nitron, whereupon the appropriate aldimine $\text{MeN}=\text{CH}(\text{C}_6\text{H}_4\text{Me-}p)$ coordinates to a Pd^{II} center. Indeed, the deoxygenation of nitrones involving metal centers is known and includes $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{Sm}$,^[32] $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -THF/ Zn ,^[33] TiCl_4/NaI ,^[34] $(\text{CF}_3\text{CO}_2)_2\text{O}/\text{NaI}$ ^[35]

reductive systems, or TiCl_3 .^[36] In the first four cases, these systems are believed to involve initial activation of the N–O group of nitron by an electrophilic reagent followed by the reduction. In the latter case, TiCl_3 plays the role of both activator and reducing reagent. Our palladium(II) systems could, in principle, reduce nitrones in a similar way insofar as they contain an activating center, i.e. Pd^{II} (Scheme 2, C), and a reducing reagent, e.g. the aldehyde $\text{O}=\text{H}$ - $\text{C}(\text{C}_6\text{H}_4\text{Me-}p)$, detected in the reaction mixture by NMR method, formed upon metal-mediated hydrolysis of the nitron.

Final Remarks

The results obtained in this work could be considered from at least two perspectives. From the viewpoint of 1,3-dipolar cycloaddition it is worthwhile to note that (i) even the rather electron-deficient nitrile PhCN in the free state does not react with the nitron (allyl anion type dipole^[2]) under the reaction conditions described above. Furthermore, a structurally similar nitron, i.e. $\text{PhCH}=\text{N}(\text{O})\text{Me}$, reacts with PhCN under harsh conditions (110 °C, 10 d) giving the corresponding oxadiazoline in 57% yield;^[37] (ii) in the synthetic experiments we did not observe a significant difference in reactivities toward the cycloaddition between the corresponding palladium(II)- (this work) and platinum(II) (ref.^[9]) complexes $[\text{MCl}_2(\text{PhCN})_2]$, albeit conditions are not strictly similar (1 d, 40 °C, in PhCN for the Pd^{II} complex and 1 d, 20–25 °C, in CH_2Cl_2 for the Pt^{II} complex). The opposite holds true for the cycloaddition of nitrile oxides (a propargyl/allenyl anion type dipole^[2]) to nitriles in $[\text{MCl}_2(\text{RCN})_2]$ complexes where the activation of RCN species, toward the cycloaddition, is higher at a Pd^{II} center. A similar trend has been observed by Lippert et al.^[38] for nucleophilic addition of water to nitriles ligated to $[\text{M}(\text{en})_2]^{2+}$ moieties; the rate of the hydrolysis found for $\text{M} = \text{Pd}^{\text{II}}$ was substantially larger than for $\text{M} = \text{Pt}^{\text{II}}$. This *difference* in activation between the two metal centers toward nitrile oxides and *similarity* toward nitrones deserves further investigations directed to the understanding of such relative behaviors and the development of a strategy for the metal-mediated 1,3-dipolar cycloaddition.

From the viewpoint of coordination of nitrones, we observed that the more labile Pd^{II} center (vs. the kinetically inert Pt^{II} and Pt^{IV} centers) reacts to a comparable degree with both dipolarophile and dipole and the latter interaction, i.e. ligation of the nitron to a Pd^{II} center (observed in this work for the first time), inhibits the 1,3-dipolar cycloaddition by coordination of the oxygen atom of the dipole.

In general, the directing of the reaction of nitriles with nitrones to a cycloaddition or a complexation route depends on a delicate balance between donor/acceptor properties of substituents at both dipolarophile and dipole, activating power of the metal center toward cycloaddition and its substitution inertness/lability toward interaction with the reactants. From this perspective the Pd^{II} center occupies an

intermediate position between such a substitutionally inert strong RCN activator as a Pt^{IV} center (where only efficient cycloaddition of both nitrones and nitrile oxides^[8] was observed) and kinetically labile (nitrile) Ti^{IV} and (nitrile) Zr^{IV} systems (where only displacement of nitriles by nitrones was reported^[15]).

Experimental Section

Materials and Instrumentation: Solvents and the nitriles were obtained from commercial sources and used as received. The complexes $[\text{PdCl}_2(\text{RCN})_2]$ ($\text{R} = \text{Me}$,^[39] Ph ^[16]) and the nitron^[40] were prepared as described previously. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 in positive ion mode. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded with a JASCO FT/IR-430 instrument in KBr pellets. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured on Bruker DPX 300 and Varian UNITY 300 spectrometers at ambient temperature.

X-ray Crystal Structure Determinations: Crystals were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 100 K or 120 K. The X-ray diffraction data was collected by a Nonius KappaCCD diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The Denzo-Scalepack^[41] program package was used for cell refinements and data reduction. The structures were solved by direct methods using the SHELXS-97 or SIR2000 programs.^[42,43] A multiscan absorption correction based on equiv. reflections (XPRED in SHELXTL v. 6.14)^[44] was applied to all of the data (the $T_{\text{min}}/T_{\text{max}}$ values were 0.7887/0.9215, 0.10130/0.16564, and 0.8169/0.9055 for **1**, **4**, and **5**, respectively). Structural refinements were carried out using SHELXL-97 with the WinGX graphical user interface.^[45,46] All of the hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data of **4** and **5** are summarized in Table 1. The selected bond lengths and angles of **4** and **5** are shown in Figure captions. The structure solution of **1** is not satisfactory and therefore the crystallographic details are only given as supplementary material (for details see below).

Table 1. Crystallographic data for complexes **4** and **5**.

	4	5
Empirical formula	$\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{N}_2\text{Pd}$	$\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2\text{Pd}_2$
f_w	443.68	580.06
Temp. [K]	100(2)	120(2)
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	6.4998(8)	10.4223(6)
b [Å]	19.8669(16)	12.0034(12)
c [Å]	7.2611(8)	8.0925(11)
α [°]	90	90
β [°]	90.734(6)	96.125(6)
γ [°]	90	90
V [Å ³]	937.56(17)	1006.6(2)
Z	2	2
$\rho_{\text{calcd.}}$ [Mg/m ³]	1.572	1.914
$\mu(\text{Mo-K}\alpha)$ [mm ⁻¹]	1.275	2.066
$R_1^{\text{[a]}}$ ($I \geq 2\sigma$)	0.0497	0.0339
$wR_2^{\text{[b]}}$ ($I \geq 2\sigma$)	0.1097	0.0636

[a] $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. [b] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

CCDC-262709 to -262711 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic Work and Characterization

Reaction of PdCl_2 with $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ in PhCN : Nitrile (0.5 mL) was added to a mixture of PdCl_2 (12 mg, 0.068 mmol) and the nitron $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ (22.4 mg, 0.150 mmol) and the suspension formed left to stand for 1 d at 45 °C. During this time the solid PdCl_2 was completely dissolved to give a yellow solution. Then the solvent was removed under vacuum at 50 °C and the oily residue was crystallized under Et_2O (five 2-mL portions) and dried under a stream of nitrogen at room temperature. The reaction can be performed starting from $[\text{PdCl}_2(\text{PhCN})_2]$ under the same reaction conditions. The reaction between PdCl_2 and $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ in PhCN is complete after 4 h under microwave irradiation (20 W, 50 °C).

$[\text{PdCl}_2\{\text{N}^a=\text{C}(\text{Ph})\text{ON}(\text{Me})\text{C}^b\text{H}(\text{C}_6\text{H}_4\text{Me-}p)\}_2(\text{N}^a-\text{C}^b)]$ (1**):** Yield 50%. $\text{C}_{32}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_2\text{Pd}$ (682.0): calcd. C 56.36, H 4.73, N 8.22; found C 58.75, H 5.03, N 8.37%. Calcd. for $\text{C}_{32}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_2\text{Pd} \cdot 2/3\text{PhCN}$: C 58.68, H 4.74, N 8.71. FAB-MS: $m/z = 647$ [$\text{M} - \text{Cl}$]⁺, 609 [$\text{M} - 2\text{HCl}$]⁺. FT-IR (KBr, selected bands): $\tilde{\nu} = 1649$ (s) $\nu(\text{C}=\text{N})\text{ cm}^{-1}$ (ref.^[15] 1632 vs. in KBr). ^1H NMR (CDCl_3): $\delta = 8.62$ (d, 2 H, $m\text{-Ar}$), 7.55 (m, 5 H, Ph), 7.32 (d, 2 H, $o\text{-Ar}$), 5.82 (br. s, 1 H, CH), 2.90 (br. s, 3 H, NMe), 2.43 (s, 3 H, $p\text{-Me}$) ppm. (ref.^[15] 8.68, 7.63, 7.48, 7.40, 7.30, 5.87, 2.95, 2.44 ppm. CDCl_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 164.74$ (C=N), 133.43, 130.46, 129.40, 128.84 and 128.41 (Ph and Ar), 93.76 (CH), 45.75 (NMe), 21.45 ($p\text{-Me}$) ppm (ref.^[15] 164.3, 139.4, 133.0, 130.4, 129.3, 129.1, 128.7, 128.6, 128.1, 122.5, 93.8, 46.0, 21.5 ppm; CDCl_3).

Among other compounds formed in the mixture we succeeded in identifying the aldehyde $p\text{-MeC}_6\text{H}_4\text{C}(\text{H})=\text{O}$ [^1H NMR (CDCl_3): $\delta = 9.94$ (s), 7.76 (d), 7.30 (d), and 2.42 (s)]. In addition, crystals of $[\text{PdCl}_2\{\text{N}(\text{Me})=\text{CH}(\text{C}_6\text{H}_4\text{Me-}p)\}_2]$ (**4**) suitable for an X-ray study were obtained by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution of the residue obtained from the reaction mixture $\text{PhCN-PdCl}_2\text{-}p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$.

Reaction of PdCl_2 (or $[\text{PdCl}_2(\text{MeCN})_2]$) and $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ in MeCN : MeCN (5 mL) was added to a mixture of PdCl_2 (12.4 mg, 0.07 mmol) (or $[\text{PdCl}_2(\text{MeCN})_2]$, 18.1 mg, 0.070 mmol) and $p\text{-MeC}_6\text{H}_4\text{CH}=\text{N}(\text{O})\text{Me}$ (21.0 mg, 0.14 mmol) and it was refluxed on stirring for 1 d, whereupon the solvent was removed in vacuo at room temperature to give a brown powder. ^1H NMR monitoring of the latter shows that the cycloaddition product is formed in 10–15% yield. The powder was treated with two 2-mL portions of Et_2O , the yellow solution was separated from the brown powder by filtration and then the filtrate was evaporated under vacuum at room temperature to give a yellow oily residue that was rapidly washed with cold Et_2O (0.5 mL) and dried again under vacuum at room temperature to give **2**. The reaction can also be performed under focused microwave irradiation (15–20 min, 100 W) and the oxadiazoline complex is formed also in ca. 10–20% yield.

$[\text{PdCl}_2\{\text{N}^a=\text{C}(\text{Me})\text{ON}(\text{Me})\text{C}^b\text{H}(\text{C}_6\text{H}_4\text{Me-}p)\}_2(\text{N}^a-\text{C}^b)] \cdot 2\text{H}_2\text{O}$ (2**):** Isolated yield is 12%. $\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_4\text{Pd}$ (557.8): calcd. C 44.50, H 5.43, N 9.43; found C 44.60, H 5.30, N 9.71. FAB-MS: $m/z = 521$ [$\text{M} - \text{HCl}$]⁺. FT-IR (KBr, selected bands): $\tilde{\nu} = 1650$ (s) $\nu(\text{C}=\text{N})\text{ cm}^{-1}$; water of crystallization was observed in the IR spectrum in well-dried KBr (3460 br). ^1H NMR (CDCl_3): $\delta = 7.47$ (d, 2 H, $m\text{-Ar}$), 7.21 (d, 2 H, $o\text{-Ar}$), 5.62 (br. s, 1 H, CH), 2.82 (br. s, 3 H, NMe), 2.45 (s, 3 H, Me), 2.40 (s, 3 H, $p\text{-Me}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 166.53$ (C=N), 139.19 ($p\text{-}$), 130.08 (C_{ipso}), 129.26 and

128.14 (*o*- and *m*-), 91.51 (br., CH), 46.09 (NMe), 21.36 (*p*-Me), 13.78 (Me) ppm.

Reaction of [PdCl₂(MeCN)₂] with *p*-MeC₆H₄CH=N(O)Me in CH₂Cl₂ and Acetone: The nitron *p*-MeC₆H₄CH=N(O)Me (0.21 mmol) was added to a solution of [PdCl₂(MeCN)₂] (26 mg, 0.10 mmol) in CH₂Cl₂ or acetone (1 mL) at room temperature. The reaction mixture became dark orange within several min, then it was allowed to stay for 2–3 h without stirring. A dark-red solution was formed, the solvent was evaporated under a stream of N₂ and the dark residue washed with Et₂O (two 2-mL portions) and dried in air and then under vacuum at room temperature. In the NMR spectrum of the residue, signals that can be attributed to the nitron complex [PdCl₂{ON(Me)=C(H)C₆H₄Me-*p*}₂] and the corresponding aldehyde *p*-MeC₆H₄C(H)O were detected. No traces of acetamide or acetic acid, corresponding to MeCN, were detected. Satisfactory elemental analyses can not be obtained because of hydrolytic and redox decomposition of the nitron complex [PdCl₂{ON(Me)=C(H)C₆H₄Me-*p*}₂]. If the reaction mixture is left standing at room temperature for 3 d, the solution becomes slightly lighter and orange-yellow crystals of [Pd₂(μ-Cl)₂{ON(Me)=C(H)C₆H₃Me-*p*}₂] are released on the top of the flask. The yield of the cyclometalated product **5** is ca. 30%.

[PdCl₂{ON(Me)=CH(C₆H₄Me-*p*)}]₂ (3**):** MS (ESI⁺): *m/z* = 441 [M – Cl], 403 [M – 2Cl – H]. FT-IR (KBr, selected bands): $\tilde{\nu}$ = 3012, 2944 (w) ν (C–H), 1601 (s) ν (C=N), 1159 (*m-s*) ν (N–O) cm^{–1}; in the free nitron 1587 (s) ν (C=N), 1167 (*m-s*) ν (N–O) cm^{–1}. ¹H NMR ([D₆]acetone): δ = 8.20 (d, 7.8 Hz, 2 H, *m*-Ar), 8.08 (s, 1 H, CH), 7.33 (d, 7.8 Hz, 2 H, *o*-Ar), 3.99 (s, 3 H, NMe), 2.39 (s, 3 H, *p*-Me) ppm. Complex **3** was also detected, by ¹H NMR method, in the reaction between the nitron and [PdCl₂(PhCN)₂].

[Pd₂(μ-Cl)₂{ON(Me)=C(H)C₆H₃Me-*p*}₂] (5**):** C₁₈H₂₀Cl₂N₂O₂Pd₂ (580.1): calcd. C 37.27, H 3.48, N 4.83; found C 37.48, H 3.60, N 4.61. FT-IR (KBr, selected bands): $\tilde{\nu}$ = 1628 (m) ν (C=N), 1582 (s) ν (C=C), 1155 (*m-s*) ν (N–O) cm^{–1}; in the free nitron 1587 (s) ν (C=N), 1167 (*m-s*) ν (N–O) cm^{–1}. The solid complex is insoluble in the most common deuterated solvents and it reacts with [D₆]DMSO to give a solution with the following spectrum, i.e. ¹H NMR ([D₆]DMSO): δ = 8.39 (s, 1 H, CH); 7.75 (d, *m*-Ar); 7.14 (d, *o*-Ar); 6.97 (s, *m*-Ar); 3.81 (s, 3 H, NMe); 2.21 (s, 3 H, *p*-Me) ppm.

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