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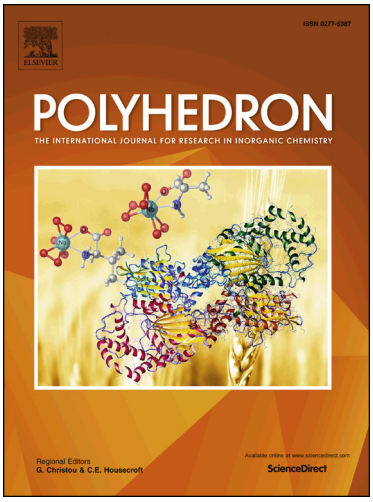


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# $Pt^{II}$ versus $Pd^{II}$-assisted [2+3] cycloadditions of nitriles and nitrone. Synthesis of nitrile-derived arylamido platinum(II) and $\Delta^4$-1,2,4-oxadiazoline palladium(II) complexes

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**ABSTRACT**

The reactions of bis(organonitrile) platinum(II) complexes *trans*-[**Pt**$Cl_2$(N≡CR)$_2$] (R = $C_6H_4$(*p*-HC=O), $CH_2C_6H_4$(*p*-$CH_3$)) with pyrroline *N*-oxide $^-O^+N{=}CHCH_2CH_2CMe_2$ afford arylamido platinum(II) complexes *trans*-[**Pt**$Cl_2${(O=CR)N=$CCH_2CH_2CMe_2NH$}$_2$] (R = $C_6H_4$(*p*-HC=O) (**1**), $CH_2C_6H_4$(*p*-$CH_3$) (**2**)). The spectral data of **1** and **2** show that the oxadiazoline rings in both cases have opened by a spontaneous N–O bond cleavage to form (*Z*)-*p*-formyl-*N*-(5,5-dimethylpyrrolidin-2-ylidene)benzamide or (*Z*)-*N*-(5,5-dimethylpyrrolidin-2-ylidene)-2-*p*-tolylacetamide ligands, respectively, where the *N*-atoms of the benzamide or acetamide moieties coordinate to platinum(II) metal centre in *trans* positions. However, the reactions of bis(organonitrile) palladium(II) complexes *trans*-[**Pd**$Cl_2$(N≡CR)$_2$] with pyrroline *N*-oxide furnish $\Delta^4$-1,2,4-oxadiazoline palladium(II) complexes *trans*-[**Pd**$Cl_2${N=C(R)ONC(H)$CH_2CH_2CMe_2$}$_2$] (R = $C_6H_4$(*p*-HC=O) (**3**), $CH_2C_6H_4$(*p*-$CH_3$) (**4**)) as the exclusive detected products. Compounds **1-4** have been characterized by IR, $^1$H, $^{13}$C NMR spectroscopy, elemental analyses, ESI$^+$-MS and also, in the case of **1**, by single crystal X-ray diffraction analysis.

*Keywords:* Platinum; Palladium; Nitriles; [2+3] Cycloadditions; N–O bond cleavage.

## 1. Introduction

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The 1,3-dipolar cycloaddition reactions of organonitriles with nitrones is one of the most important routes for the preparation of $\Delta^4$-1,2,4-oxadiazolines [1,2]. However, there are some difficulties associated with the use of nitriles as only organonitriles bearing an electron acceptor group react with nitrones under harsh reaction conditions [3,4]. The coordination of organonitriles to a platinum or palladium metal centre becomes a useful strategy and facile metal-assisted route for the preparation of a variety of products which are difficult to synthetize directly by pure organic chemistry [1]. The N–O bond cleavage of the $\Delta^4$-1,2,4-oxadiazoline ligands can be promoted by thermal heating to afford ketoimine palladium(II) complexes [5]. However, the $\Delta^4$-1,2,4-oxadiazoline rings have been opened by N–O bond cleavage at room temperature [6] or under heating [7] to form *trans* pyrrolylbenzamide palladium(II) complexes. On the other hand, it was found that the platinum(II) complexes $[PtCl_2(RCN)_2]$ (R = $CH_2Cl$, $CH_2CO_2Me$) react with a cyclic nitrone to furnish the ketoimino platinum(II) complexes *via* one-pot reaction involving spontaneous N–O bond cleavage [8].

In this work, we would like to understand the difference between using platinum(II) and palladium(II) metal centre as a Lewis acid for the 1,3-dipolar cycloaddition reaction of pyrroline *N*-oxide and nitriles such as *p*-cyanobenzaldehyde and *p*-tolylacetonitrile. Hence, we found that the reactions of *trans*-[**Pt**$Cl_2(N{\equiv}CR)_2$] with pyrroline *N*-oxide afford *trans*-[**Pt**$Cl_2\{(O{=}CR)N{=}CCH_2CH_2CMe_2NH\}_2$] complexes (R = $C_6H_4$(*p*-HC=O) (**1**), $CH_2C_6H_4$(*p*-$CH_3$) (**2**)) as a result of the N–O bond cleavage of the oxadiazoline rings. In contrast, the reactions of *trans*-[**Pd**$Cl_2(N{\equiv}CR)_2$] with pyrroline *N*-oxide furnish *trans*-[**Pd**$Cl_2\{N{=}C(R)ONC(H)CH_2CH_2CMe_2\}_2$] complexes (R = $C_6H_4$(*p*-HC=O) (**3**), $CH_2C_6H_4$(*p*-$CH_3$) (**4**)) as the exclusive detected products.

## 2. Experimental section

### *2.1. General methods*

The bis(*p*-cyanobenzaldehyde) platinum(II) and palladium(II) complexes *trans*-$[MCl_2(N{\equiv}CC_6H_4(p\text{-}HC{=}O))_2]$ (M = Pt, Pd) and bis(*p*-tolylacetonitrile) platinum(II) and palladium(II) complexes *trans*-$[MCl_2(N{\equiv}CCH_2C_6H_4(p\text{-}CH_3))_2]$ (M = Pt, Pd) were previously synthesized by one of us [2b,9]. Moreover, the $\Delta^4$-1,2,4-oxadiazoline palladium(II) complex (**3**) was also reported by one of us in our previous work [2b].

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Infrared spectra (4000-400 $cm^{-1}$) were recorded on an Alpha Bruker FT-IR instrument in KBr pellets and the wavenumbers are in $cm^{-1}$. $^{1}H$ and $^{13}C$ NMR spectra (in $CDCl_3$) were measured on Bruker Avance III HD 600 MHz (Ascend™ Magnet) spectrometer at ambient temperature. High resolution electrospray ionization mass spectrometry (ESI-MS) or high resolution electron ionization (EI) mass spectra were recorded using an impact II mass spectrometer from Bruker or Agilent Q-TOF 6520 instrument, respectively; all mass spectrometry are reported as *m/z*.

### *2.2. Reaction of trans-[$PtCl_2(N{\equiv}CR)_2$] (R = $C_6H_4$(p-HC=O), $CH_2C_6H_4$(p-$CH_3$)) with pyrroline N-oxide $^{-}O^{+}N{=}CHCH_2CH_2CMe_2$*

Pyrroline *N*-oxide (21.2 mg, 0.187 mmol) was added to a solution of *trans*-[$PtCl_2(N{\equiv}CC_6H_4$(*p*-HC=O))$_2$] (45.0 mg, 0.085 mmol) or *trans*-[$PtCl_2(N{\equiv}CCH_2C_6H_4$(*p*-$CH_3$))$_2$] (44.9 mg, 0.085 mmol) in chloroform (10 mL), and the reaction mixture was stirred at room temperature for 2 h, whereupon the solvent was removed *in vacuo*. The crude residue was purified by column chromatography on silica (chloroform as the eluent, 50 mL), followed by evaporation of the solvent *in vacuo* to give the final *trans*-dichloridobis[(*Z*)-*p*-formyl-*N*-(5,5-dimethylpyrrolidin-2-ylidene)benzamide] platinum(II) complex (**1**) [57.7 mg, 90% yield] and *trans*-dichloridobis[(*Z*)-*N*-(5,5-dimethylpyrrolidin-2-ylidene)-2-*p*-tolylacetamide] platinum(II) complex (**2**) [57.1 mg, 89% yield], respectively.

During the crystallization of **1** the free *p*-cyanobenzaldehyde has been co-crystallized with the complex **1**, and it has been confirmed by electron ionization (EI) mass spectrometry, *m/z*: 131 $[M]^{+}$ (Supplementary data). The presence of *free p*-cyanobenzaldehyde in the crystals of **1** is due to its initial existence (in a small amount) along with its coordinated platinum complex *trans*-[$PtCl_2(N{\equiv}CC_6H_4$(*p*-HC=O))$_2$]. After the [2+3] cycloaddition reaction, we attempted to obtain single crystals directly from the reaction mixture (before its purification by column chromatography on silica), which explains the presence of *free p*-cyanobenzaldehyde in the crystal of complex **1**.

#### *2.2.1. Trans-[$PtCl_2${(O=$CC_6H_4$(p-HC=O))N=$CCH_2CH_2CMe_2NH$}$_2$] (**1**)*

IR ($cm^{-1}$): 1699 υ(NC=O), 1654 υ(N=C), 3258 υ(NH). $^{1}H$ NMR ($CDCl_3$), $\delta$: 1.31 (s, 12H, $CH_3$), 1.74 (s, 4H, $CH_2$), 2.98 (s, 4H, $CH_2$), 8.02 (d, $J_{HH}$ 8.1 Hz, 4H, $CH_{aromatic}$),

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8.18 (d, $J_{HH}$ 8.1 Hz, 4H, C*H*$_{aromatic}$), 10.13 (s, 2H, *H*C=O). $^{13}$C NMR ($CDCl_3$), *δ*: 28.3 (*C*H$_3$), 128.8, 129.9, 137.1, 145.4 (C$_{aromatic}$), 174.5 (N*C*=O), 191.7 (H*C*=O). *The other signals cannot be detected by $^{13}$C NMR even after a long accumulation period.* Anal. Calcd for $C_{28}H_{32}N_4O_4Cl_2Pt$ (753.14): C, 44.57; H, 4.27; N, 7.43. Found: C, 44.81; H, 4.63; N, 7.78. ESI$^+$-MS, *m/z*: 753.12 [M]$^+$.

*2.2.2. Trans-[PtCl$_2${(O=CCH$_2$C$_6$H$_4$(p-CH$_3$))N=CCH$_2$CH$_2$CMe$_2$NH}$_2$] (**2**)*

IR (cm$^{-1}$): 1669 υ(NC=O), 1577 υ(N=C), 3417 υ(NH). $^1$H NMR ($CDCl_3$), *δ*: 1.36 (s, 12H, C*H*$_3$), 1.99 (m, 4H, C*H*$_2$), 2.37 (m, 6H, C*H*$_3$), 4.00 (t, $J_{HH}$ 7.4 Hz, 4H, C*H*$_2$), 5.09 (s, 4H, C*H*$_2$), 7.15-7.22 (m, 8H, C*H*$_{aromatic}$), 10.89 (bs, 2H, N*H*). $^{13}$C NMR ($CDCl_3$), *δ*: 21.1 (*C*H$_3$), 28.7 (*C*H$_3$), 32.9 (*C*H$_2$), 47.2 (*C*H$_2$), 65.1 (*C*-NH), 129.1, 130.0, 131.9, 136.6 (C$_{aromatic}$), 173.6 (N=*C*), 184.6 (N*C*=O). Anal. Calcd for $C_{30}H_{40}N_4O_2Cl_2Pt$ (753.22): C, 47.75; H, 5.34; N, 7.42. Found: C, 48.10; H, 5.55; N, 7.68. ESI$^+$-MS, *m/z*: 753.16 [M]$^+$.

*2.3. Reaction of trans-[PdCl$_2$(N≡CCH$_2$C$_6$H$_4$(p-CH$_3$))$_2$] with pyrroline N-oxide $^-$O$^+$N=CHCH$_2$CH$_2$CMe$_2$*

Pyrroline *N*-oxide (21.2 mg, 0.187 mmol) was added to a solution of *trans*-[PdCl$_2$(N≡CCH$_2$C$_6$H$_4$(*p*-CH$_3$))$_2$] (37.4 mg, 0.085 mmol) in chloroform (10 mL), and the reaction mixture was stirred at room temperature for 2 h, whereupon the solvent was removed *in vacuo*. The crude residue was purified by column chromatography on silica (chloroform as the eluent, 50 mL), followed by evaporation of the solvent *in vacuo* to give the final Δ$^4$-1,2,4-oxadiazoline palladium(II) complex (**4**) as the exclusive detected product [45.3 mg, 80% yield].

*2.3.1. Trans-[PdCl$_2${N=C(CH$_2$C$_6$H$_4$(p-CH$_3$))ONC(H)CH$_2$CH$_2$CMe$_2$}$_2$] (**4**)*

IR (cm$^{-1}$): 1659 υ(C=N). $^1$H NMR ($CDCl_3$), *δ*: 0.98 and 1.01 (two s, 6H, two C*H*$_3$), 1.07 and 1.09 (two s, 6H, two C*H*$_3$), 1.26-1.32 (m, 2H, C*H*$_2$), 1.55-1.70 (m, 6H, three C*H*$_2$), 2.29 and 2.31 (two s, 6H, two C*H*$_3$), 2.93-2.97 (m, 2H, C*H*$_2$), 4.21-4.27 (m, 2H, C*H*$_2$), 5.46 (t, $J_{HH}$ 5.4 Hz, 2H, N-C*H*-N), 7.12-7.22 (m, 4H, C*H*$_{aromatic}$), 7.34-7.39 (m, 4H, C*H*$_{aromatic}$). $^{13}$C NMR ($CDCl_3$), *δ*: 21.1, 22.2 and 27.2 (*C*H$_3$), 30.2, 33.5 and 33.9 (*C*H$_2$), 69.9 (Me$_2$*C*-N), 88.4 (N-*C*H-N), 127.8, 129.4, 129.7 and 137.3 (C$_{aromatic}$), 167.5 and

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167.6 (*C*(O)=N). Anal. Calcd for $C_{30}H_{40}N_4O_2Cl_2Pd$ (664.16): C, 54.10; H, 6.05; N, 8.41. Found: C, 54.25; H, 6.17; N, 8.55. ESI$^+$-MS, *m/z*: 663.02 [M-H]$^+$.

### *2.4. X-ray structure determinations*

The crystals of **1** were obtained by slow evaporation of its chloroform solution. The crystals were measured on a D8 QUEST Bruker Diffractometer. The *Apex3* [10] program package was used for cell refinements and data reductions. Multi-scan absorption correction (*SADABS*) [11] was applied to the intensities before structure solution. The structure was solved using the *SHELXT* [12] software. Structural refinement was carried out using *SHELXL-2017* [12]. The NH hydrogen atom was located from the difference Fourier map and refined isotropically. Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95–1.00 Å, and *U*iso = 1.2–1.5 *U*eq (parent atom). The crystallographic details are summarized in Table 1.

**Table 1**. Crystal Data of **1**.

| | **1** |
|---|---|
| empirical formula | $C_{28}H_{32}Cl_2N_4O_4Pt$, $C_8H_5NO$, $2(CHCl_3)$ |
| Fw | 1124.43 |
| temp (K) | 115(2) |
| $\lambda$(Å) | 0.71073 |
| cryst syst | Triclinic |
| space group | P-1 |
| *a* (Å) | 8.981(5) |
| *b* (Å) | 10.468(5) |
| *c* (Å) | 13.049(8) |
| $\alpha$(°) | 100.680(15) |
| $\beta$(°) | 105.685(15) |
| $\gamma$(°) | 103.623(14) |
| *V* (Å$^3$) | 1106.5(11) |
| Z | 1 |
| $\rho_{calc}$ (Mg/m$^3$) | 1.688 |
| $\mu$(K$\alpha$) (mm$^{-1}$) | 3.701 |
| No. reflns. | 25321 |
| Unique reflns. | 4054 |
| GOOF (F$^2$) | 1.07 |
| $R_{int}$ | 0.040 |
| R1$^a$ ($I \geq 2\sigma$) | 0.0198 |
| wR2$^b$ ($I \geq 2\sigma$) | 0.0424 |

$^a$ $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

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## 3. Results and discussion

### *3.1. Synthesis of platinum(II) complexes (**1**) and (**2**)*

The reaction of bis(*p*-cyanobenzaldehyde) platinum(II) complex *trans*-[$PtCl_2(N{\equiv}CC_6H_4(p\text{-}HC{=}O))_2$] with pyrroline *N*-oxide $^{-}O^{+}N{=}CHCH_2CH_2CMe_2$, in $CHCl_3$ at room temperature for 2 h, affords *trans*-dichloridobis[(*Z*)-*p*-formyl-*N*-(5,5-dimethylpyrrolidin-2-ylidene)benzamide] platinum(II) complex *trans*-[$PtCl_2\{(O{=}CC_6H_4(p\text{-}HC{=}O))N{=}CCH_2CH_2CMe_2NH\}_2$] (**1**) as the exclusive detected product (Scheme 1, reaction *a*), instead of the expected $\Delta^4$-1,2,4-oxadiazoline platinum(II) complex *trans*-[$PtCl_2\{N{=}C(C_6H_4(p\text{-}HC{=}O))ONC(H)CH_2CH_2CMe_2\}_2$] which has never been detected by NMR spectroscopy (Scheme 1, reaction *b*). Complex **1** has been characterized by IR, $^1H$, $^{13}C$ NMR spectroscopy, elemental analysis, $ESI^+$-MS, and also by single crystal X-ray diffraction analysis which shows that the $\Delta^4$-1,2,4-oxadiazoline rings have opened by spontaneous N–O bond cleavage to form (*Z*)-*p*-formyl-*N*-(5,5-dimethylpyrrolidin-2-ylidene)benzamide ligands where both *N*-atoms of the benzamide moieties coordinate to platinum(II) metal centre in *trans* positions.

The IR spectrum of complex **1** showed strong υ(NC=O) and υ(N=C) vibrations at 1699 and 1654 $cm^{-1}$, respectively, and υ(NH) at 3258 $cm^{-1}$. In the $^{13}C$ NMR spectrum, the N*C*=O resonances are detected at $\delta$ 174.5 ppm and confirm the N–O ring cleavage.

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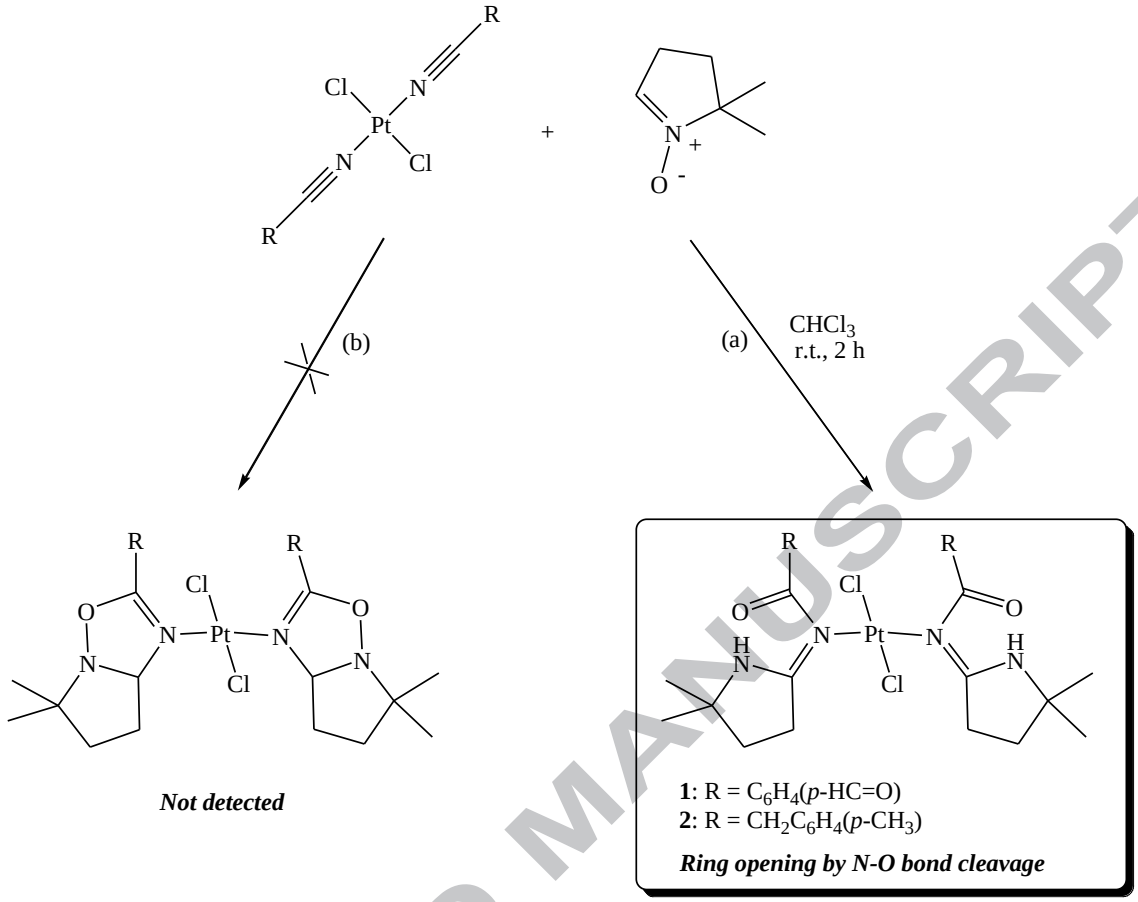


**Scheme 1**

On the other hand, the reaction of bis(*p*-tolylacetonitrile) platinum(II) complex *trans*-[$PtCl_2(N{\equiv}CCH_2C_6H_4(p\text{-}CH_3))_2$] with pyrroline *N*-oxide, in $CHCl_3$ at room temperature for 2 h, furnishes *trans*-dichloridobis[(*Z*)-*N*-(5,5-dimethylpyrrolidin-2-ylidene)-2-*p*-tolylacetamide] platinum(II) complex *trans*-[$PtCl_2\{(O{=}CCH_2C_6H_4(p\text{-}CH_3))N{=}CCH_2CH_2CMe_2NH\}_2$] (**2**) as the exclusive detected product (Scheme 1, reaction *a*). Also in this case, the expected $\Delta^4$-1,2,4-oxadiazoline platinum(II) complex *trans*-[$PtCl_2\{N{=}C(CH_2C_6H_4(p\text{-}CH_3))ONC(H)CH_2CH_2CMe_2\}_2$] has never been observed by NMR spectroscopy (Scheme 1, reaction *b*). Complex **2** has been characterized by IR, $^1H$, $^{13}C$ NMR spectroscopy, elemental analysis and $ESI^+$-MS which shows that the $\Delta^4$-1,2,4-oxadiazoline rings have opened by spontaneous N–O bond cleavage to form (*Z*)-*N*-(5,5-dimethylpyrrolidin-2-ylidene)-2-*p*-tolylacetamide ligands.

The IR spectrum of complex **2** showed strong υ(NC=O) and υ(N=C) vibrations at 1669 and 1577 $cm^{-1}$, respectively, and υ(NH) at 3417 $cm^{-1}$. In the $^1H$ NMR spectrum, the proton N*H* resonance is detected at $\delta$ 10.9 ppm. In the $^{13}C$ NMR spectrum, the N=*C* and

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N*C*=O resonances are detected at $\delta$ 173.6 and 184.6 ppm, respectively, and confirm the N–O ring cleavage.

### *3.2. X-ray structure crystallography*

In the crystal structure, *trans*-dichloridobis[(*Z*)-*p*-formyl-*N*-(5,5-dimethylpyrrolidin-2-ylidene)benzamide] platinum(II) complex **1** the central $Pt^{II}$ metal atom displays a distorted square-planar coordination (Fig. 1, Table 2). The two Cl atoms and the two N atoms of imine groups forming the square-planar coordinated to the central $Pt^{II}$ atom. In **1**, the two Cl atoms and the two N atoms are *trans* with respect to each other.

The TELP Figure of structure **1** is shown in Fig. 1. The key non-covalent intermolecular interactions involving the platinum complex were located by using a Hirschfeld surface analysis. The Hirschfeld surface ($d_{norm}$) [13] is shown in Fig. 2. In structure **1**, two neighbouring platinum molecules are connected *via* two equivalent N-H···O hydrogen bonds (contact **A** in Fig. 2. Structural details are given in Table 2). The $CH_2$-group of the five-membered ring (C14) is acting as a weak H-bond donor for the chloride of $CHCl_3$ (contact **E** in Fig. 2). Simultaneously, the H-atom of the $CHCl_3$ molecule is acting as a donor for the O(2) oxygen of the Pt molecule (**D**). One of the methyl groups on the five-membered ring (C12) is involved in two CH-π interactions. The methyl group is contacted both with the *p*-formylbenzamide group of the neighbouring Pt complex (**B**) and with the free *p*-cyanobenzaldehyde molecule (**C**). The solvent of crystallization *i.e.* $CHCl_3$, is acting also as halogen bond donor for the platinum coordinated Cl(1) ligand (**F**). The Cl···Cl distance of 3.295(2) Å is equal to 5.9% contraction of the contact compared to the sum of the Bondi's van der Waals radii [14]. Such a small value is indicative for relatively weak halogen bond.

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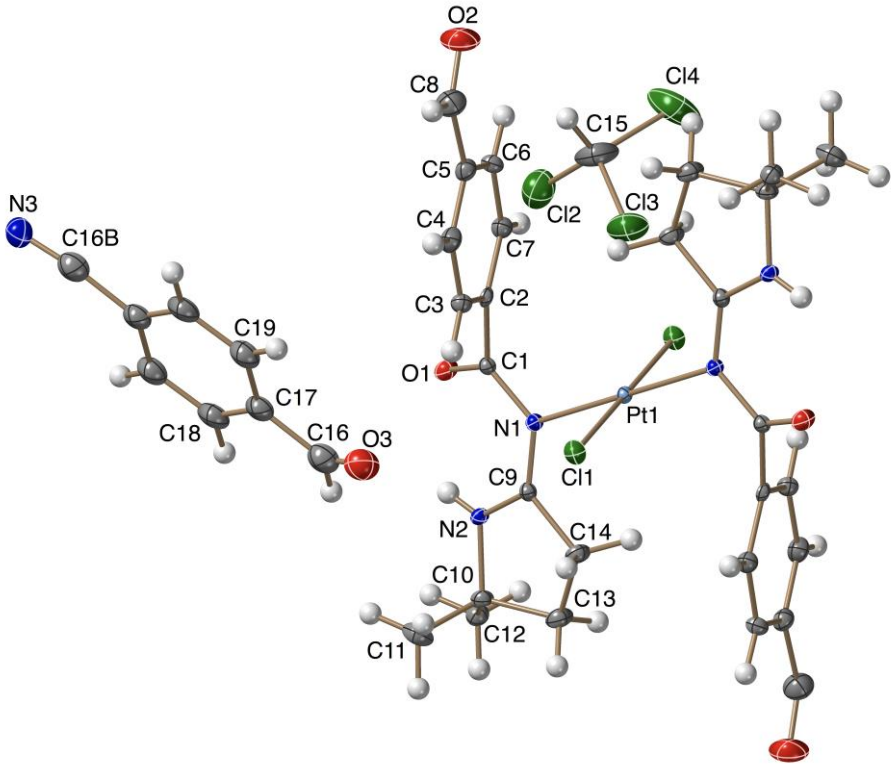


**Fig. 1**. The TELP drawing (50% probability level) of **1**. The halogen bond contact between the metal complex and $CHCl_3$ solvent molecule: Cl(1)···Cl(3): 3.295(2) Å, C(15)-Cl(3)···Cl(1): 166.82(11)°, Pt(1)-Cl(1)···Cl(3): 141.61(4)°.

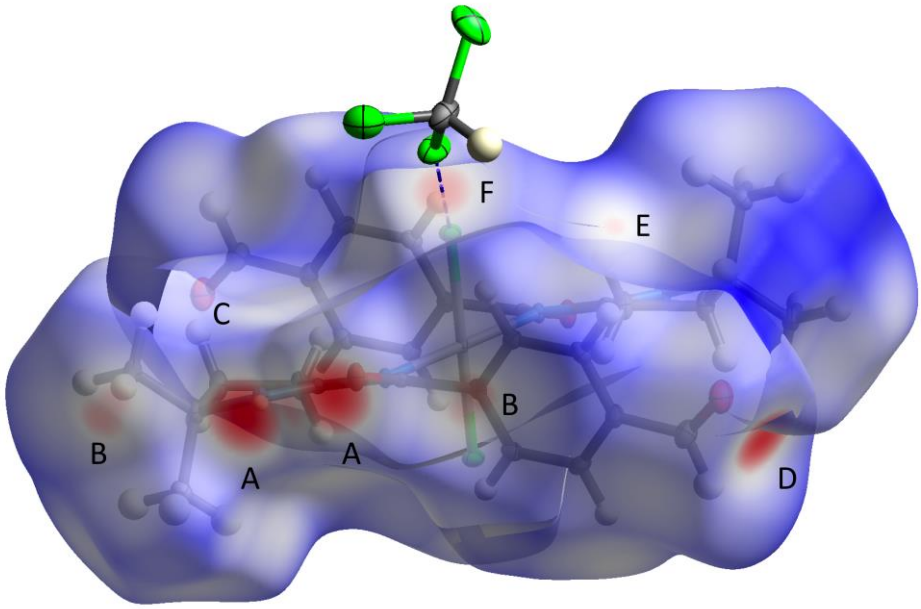


**Fig. 2**. Hirschfeld surface ($d_{norm}$) of **1**. The figure is generated by CrystalExplorer software [13]. Contacts: **A**: Hydrogen bond between N(2) and O(1), **B**: CH-π interaction

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between C(12) and the coordinated *p*-formylbenzamide group from the neighboring metal complex. **C**: CH-π interaction between C(12) and the noncoordinated *p*-cyanobenzaldehyde molecule. **D**: Weak H-bond between $CHCl_3$ (donor) and O(2) of the noncoordinated molecule. **E**: Weak H-bond between C(14) and Cl(4). **F**: Halogen bond between the chloroform (Cl(3) as donor) and the Cl(1) ligand.

**Table 2**. The intermolecular non-covalent contacts involving complex **1**.

| | Contact | d(D-H) (Å) | d(H···A) (Å) | d(D···A) (Å) | <DH···A (°) |
|---|---|---|---|---|---|
| H-Bond **A** | N(2)-H(2)···O(1)$^{\#1}$ | 0.78(3) | 2.25(3) | 2.990(3) | 159(3) |
| H-Bond **D** | C(15)-H(15)···O(2)$^{\#2}$ | 1.00 | 2.19 | 3.180(4) | 171.8 |
| H-Bond **E** | C(14)-H(14B) )···Cl(4)$^{\#3}$ | 0.99 | 2.84 | 3.647(3) | 138.6 |
| | Contact | d(C-H) (Å) | d(H···C) (Å) | d(C···C) (Å) | <C-H···C (°) |
| CH-π **B** | C(12)-H(12C)···C(2)$^{\#4}$ | 0.98 | 2.790 | 3.769 | 178.2 |
| | C(12)-H(12C)···C(7)$^{\#4}$ | 0.98 | 2.691 | 3.584 | 151.7 |
| CH-π **C** | C(12)-H(12A)···C(17)$^{\#5}$ | 0.98 | 2.844 | 3.819 | 173.0 |
| | C(12)-H(12A)···C(18)$^{\#5}$ | 0.98 | 2.854 | 3.782 | 158.1 |
| | Contact | Pt(1)-Cl(1) | Cl(1)···Cl(3) | C(15)-Cl(3)···Cl(1) | Pt(1)-Cl(1)···Cl(3) |
| Halogen bond **F** | Pt(1)-Cl(1) )···Cl(3) | 2.3031(12) | 3.295(2) | 166.82(11) | 141.61(4) |

Symmetry transformations used to generate equivalent atoms: #1: -x+2,-y+2,-z+1, #2: x+1,y,z+1, #3: -x+2,-y+1,-z+2, 4: x, -1+y, z, #5: 2-x, 1-y, 1-z.

### *3.3. Synthesis of palladium(II) complexes (**3**) and (**4**)*

In our previous work [2b], we have shown that the reaction of pyrroline *N*-oxide with bis(*p*-cyanobenzaldehyde) palladium(II) complex *trans*-[$PdCl_2(N{\equiv}CC_6H_4(p\text{-}HC{=}O))_2$] afforded $\Delta^4$-1,2,4-oxadiazoline palladium(II) complex *trans*-[$PdCl_2\{N{=}C(C_6H_4(p\text{-}HC{=}O))ONC(H)CH_2CH_2CMe_2\}_2$] (**3**). Hence, the reaction of bis(*p*-tolylacetonitrile) palladium(II) complex *trans*-[$PdCl_2(N{\equiv}CCH_2C_6H_4(p\text{-}CH_3))_2$] with pyrroline *N*-oxide, in $CHCl_3$ at room temperature for 2 h, furnishes $\Delta^4$-1,2,4-oxadiazoline palladium(II) complex *trans*-[$PdCl_2\{N{=}C(CH_2C_6H_4(p\text{-}CH_3))ONC(H)CH_2CH_2CMe_2\}_2$] (**4**) as the exclusive detected product (Scheme 1, reaction *a*). In this case, the cleavage of the N–O bond has not observed, and *trans*-dichloridobis[(*Z*)-*N*-(5,5-dimethylpyrrolidin-2-ylidene)-2-*p*-tolylacetamide] palladium(II) complex *trans*-[$PdCl_2\{(O{=}CCH_2C_6H_4(p\text{-}$

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$CH_3$))N=$CCH_2CH_2CMe_2NH\}_2$] has never been detected by NMR spectroscopy (Scheme 1, reaction *b*).

Complex **4** has been characterized by IR, $^1$H, $^{13}$C NMR spectroscopy, elemental analysis and ESI$^+$-MS which shows that the *trans* $\Delta^4$-1,2,4-oxadiazoline rings have been formed without further N–O bond cleavage. The IR spectrum of complex **4** showed strong υ(N=C) vibration at 1659 cm$^{-1}$. In the $^1$H NMR spectrum, the proton N-C*H*-N resonance is detected at $\delta$ 5.46 ppm. In the $^{13}$C NMR spectrum, the *C*(O)=N resonances are detected at $\delta$ 167.5 and 167.6 ppm, and confirm the formation of the $\Delta^4$-1,2,4-oxadiazoline rings.

In contrast with the oxadiazoline complexes formed by reaction of acyclic nitrones with coordinated organonitriles, which exhibit two sets of signals corresponding to 1:1 diastereoisomeric mixtures [2d,15], complex **4** displays only one set of NMR signals which indicate that the [2+3] cycloaddition reactions proceed with high diastereoselectivity leading to the formation of a pair of enantiomers [(*R*,*R*)/(*S*,*S*)], whereas in case of complex **4** two signals with very close chemical shift values ($\Delta\delta$ ~ 0.11 ppm) were observed, which belong to two oxadiazoline moieties with a different [(*R*,*S*)/(*S*,*R*)] configuration [6]. The structure of the cyclic nitrone (pyrroline *N*-oxide) $^-O^+N=CHCH_2CH_2CMe_2$ offers a more rigid conformation (*E*) than in the case of the acyclic ones $^-O^+N(Me)=C(H)(Ar)$ preventing one of the nitrone sides from the reaction, thus promoting the selectivity [2b,6,16].

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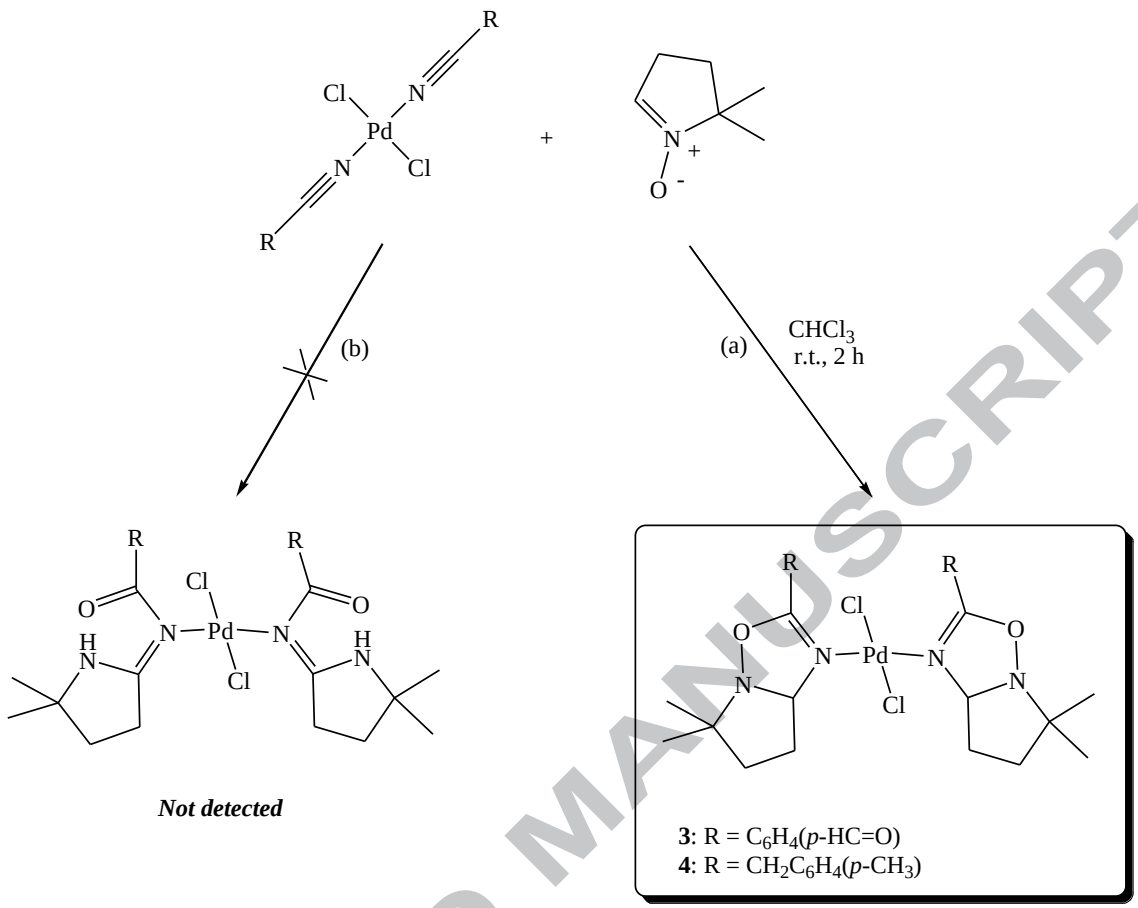


**Scheme 2**

## 4. Conclusions

The results of this work show that the facile $Pt^{II}$-assisted [2+3] cycloaddition reaction of cyclic nitrone (pyrroline *N*-oxide) with organonitrile RCN ligands (R = $C_6H_4$(*p*-HC=O), $CH_2C_6H_4$(*p*-$CH_3$)), at room temperature, occurs with N–O bond rupture to give new $Pt^{II}$ complexes *via* a single-pot reaction. Hence, we succeeded to prepare *trans*-[**Pt**$Cl_2${(O=CR)N=$CCH_2CH_2CMe_2$NH}$_2$] complexes (R = $C_6H_4$(*p*-HC=O) (**1**), $CH_2C_6H_4$(*p*-$CH_3$) (**2**)). However, the expected $\Delta^4$-1,2,4-oxadiazoline platinum(II) complexes *trans*-[**Pt**$Cl_2${N=C(R)ONC(H)$CH_2CH_2CMe_2$}$_2$] (R = $C_6H_4$(*p*-HC=O), $CH_2C_6H_4$(*p*-$CH_3$)) have never been detected by NMR spectroscopy or X-ray crystallography. On the other hand, using palladium(II) metal centre instead of platinum(II), under the same experimental conditions, we succeeded to isolate $\Delta^4$-1,2,4-oxadiazoline palladium(II) complexes *trans*-[**Pd**$Cl_2${N=C(R)ONC(H)$CH_2CH_2CMe_2$}$_2$] (R = $C_6H_4$(*p*-HC=O) (**3**), $CH_2C_6H_4$(*p*-$CH_3$) (**4**)) as the exclusive products. Hence the

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metal centre plays a key role in obtaining products with or without N–O bond cleavage. The obtained results when using $Pt^{II}$ centre are in good agreement with those observed by other groups [8]. However, except in the case of 2-cyanopyridine [17], the use of $Pd^{II}$ centre for [2+3] cycloaddition of cyclic nitrone with nitriles, at room temperature, affords in all cases $\Delta^4$-1,2,4-oxadiazoline palladium(II) complexes [2b,5,6].

**Appendix A. Supplementary data**

CCDC 1864425 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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**References**

[1] N.A. Bokach, M.L. Kuznetsov, V.Yu. Kukushkin, 1,3-Dipolar cycloaddition of nitrone-type dipoles to uncomplexed and metal-bound substrates bearing the CN triple bond, Coord. Chem. Rev. 255 (2011) 2946-2967.

[2] (a) J. Lasri, S.M. Soliman, M.A. Januário Charmier, M. Ríos-Gutiérrez, L.R. Domingo, Synthesis, molecular structure and stability of fused bicyclic $\Delta^4$-1,2,4-oxadiazoline Pt(II) complexes, Polyhedron 98 (2015) 55-63; (b) J. Lasri, Palladium(II)-assisted [2+3] cycloaddition of nitrones to organonitriles: Synthesis of 2,3-dihydropyrrolo[1,2-a]quinazolin-5-one and $\Delta^4$-1,2,4-oxadiazoline derivatives, Polyhedron 57 (2013) 20-23; (c) R.R. Fernandes, J. Lasri, M.F.C. Guedes da Silva, A.M.F. Palavra, J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, Oxadiazoline and ketoimine palladium(II) complexes as highly efficient catalysts for Suzuki–Miyaura cross-coupling reactions in supercritical carbon dioxide, Adv. Synth. Catal. 353 (2011) 1153-1160; (d) J. Lasri, M.A. Januário Charmier, M. Haukka, A.J.L. Pombeiro,

ACCEPTED MANUSCRIPT



Stereospecific synthesis of polysubstituted *E*-Olefins by reaction of acyclic nitrones with free and platinum(II) coordinated organonitriles, J. Org. Chem. 72 (2007) 750-755; (e) J. Lasri, M.A. Januário Charmier, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Mixed unsymmetric oxadiazoline and/or imine platinum(II) complexes, Dalton Trans. (2007) 3259-3266.

[3] L. Eberson, J.J. McCullough, C.M. Hartshorn, M.P. Hartshorn, 1,3-Dipolar cycloaddition of α-phenyl-*N*-*tert*-butylnitrone (PBN) to dichloro- and dibromo-malononitrile, chlorotricyanomethane and tetracyanomethane. Structure of products and kinetics of their formation, J. Chem. Soc., Perkin Trans. 2, 1 (1998), 41-48.

[4] J. Lasri, M.N. Kopylovich, M.F.C. Guedes da Silva, M.A. Januário Charmier, A.J.L. Pombeiro, Metal-free and $Pd^{II}$-Promoted [2+3] cycloadditions of a cyclic nitrone to phthalonitriles: syntheses of oxadiazolines as well as phthalamide–$Pd^{II}$ and dihydropyrrolyl-iminoisoindolinone–$Pd^{II}$ complexes with high catalytic activity in Suzuki–Miyaura cross-coupling reactions, Chem. Eur. J. 14 (2008) 9312-9322.

[5] J. Lasri, T.C.O. Mac Leod, A.J.L. Pombeiro, Oxadiazoline and ketoimine palladium(II) complexes supported on a chitosan membrane and their catalytic activity for the microwave-assisted Suzuki–Miyaura cross-coupling in water, Appl. Catal. A: Gen. 397 (2011) 94-102.

[6] J. Lasri, M.F.C. Guedes da Silva, M.N. Kopylovich, S. Mukhopadhyay, M.A. Januário Charmier, A.J.L. Pombeiro, $Pd^{II}$-promoted [2+3] cycloaddition of pyrroline *N*-oxide to organonitriles. Application of ($\Delta^4$-1,2,4-oxadiazoline)-$Pd^{II}$ complexes in the Suzuki–Miyaura reaction, Dalton Trans. (2009) 2210-2216.

[7] J. Lasri, N.E. Eltayeb, M. Haukka, B.A. Babgi, Crystal structure of *trans*-dichloridobis[*N*-(5,5-dimethyl-4,5-dihydro-3*H*-pyrrol-2-yl-*κN*)acetamide]palladium(II) dihydrate, Acta Cryst. E73 (2017) 528-530.

[8] M.A. Januário Charmier, M. Haukka, A.J.L. Pombeiro, Unprecedented single-pot synthesis of nitrile-derived ketoimino platinum(II) complexes by ring opening of $\Delta^4$-1,2,4-oxadiazolines, Dalton Trans. (2004) 2741-2745.

[9] J. Lasri, B. Pedras, M. Haukka, M.N. Berberan-Santos, Pt(II) and Pd(II)-assisted coupling of nitriles and 1,3-diiminoisoindoline: Synthesis and luminescence properties of (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) and Pd(II) complexes, Polyhedron 133 (2017) 195-202.

[10] Bruker AXS, APEX3 – Software Suite for Crystallographic Programs (2016). Bruker AXS, Inc.: Madison, WI, USA.

ACCEPTED MANUSCRIPT



[11] G.M. Sheldrick, (2016). SADABS - Bruker Nonius scaling and absorption correction, Bruker AXS, Inc.: Madison, Wisconsin, USA, 2.

[12] G.M. Sheldrick, Integrated space-group and crystal-structure determination, Acta Cryst. C71 (2015) 3-8.

[13] M.J. Turner, J.J. McKinnon, S.K. Wolff, D.J. Grimwood, P.R. Spackman, D. Jayatilaka, M.A. Spackman, CrystalExplorer17 (2017). University of Western Australia.

[14] A. Bondi, van der Waals Volumes and Radii, J. Phys. Chem. 68 (1964) 441-451.

[15] (a) G. Wagner, M. Haukka, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, V.Yu. Kukushkin, [2+3] Cycloaddition of nitrones to platinum-bound organonitriles: Effect of metal oxidation state and of nitrile substituent, Inorg. Chem. 40 (2001) 264-271; (b) G. Wagner, A.J.L. Pombeiro, V.Yu. Kukushkin, Platinum(IV)-assisted [2+3] cycloaddition of nitrones to coordinated organonitriles. Synthesis of $\Delta^4$-1,2,4-oxadiazolines, J. Am. Chem. Soc. 122 (2000) 3106-3111.

[16] M.A. Januário Charmier, V.Yu. Kukushkin, A.J.L. Pombeiro, Microwave-assisted [2+3] cycloaddition of nitrones to platinum-(II) and -(IV) bound organonitriles, Dalton Trans. (2003) 2540-2543.

[17] M.N. Kopylovich, J. Lasri, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Single-pot template transformations of cyanopyridines on a $Pd^{II}$ centre: Syntheses of ketoimine and 2,4-dipyridyl-1,3,5-triazapentadiene palladium(II) complexes and their catalytic activity for microwave-assisted Suzuki–Miyaura and Heck reactions, Dalton Trans. (2009) 3074-3084.

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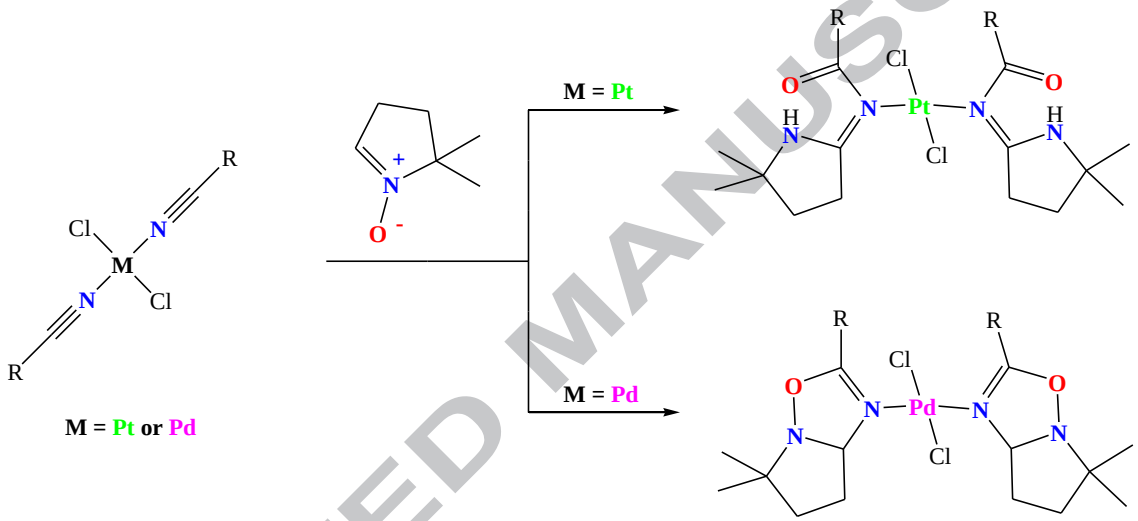
## Graphical abstract

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## Synopsis

The reactions of *trans*-[**Pt**$Cl_2$(N≡CR)$_2$] with pyrroline *N*-oxide afford arylamido platinum(II) complexes *trans*-[**Pt**$Cl_2${(O=CR)N=$CCH_2CH_2CMe_2$NH}$_2$] *via* one-pot reaction involving spontaneous N–O bond cleavage. However, the reactions of *trans*-[**Pd**$Cl_2$(N≡CR)$_2$] with pyrroline *N*-oxide furnish $\Delta^4$-1,2,4-oxadiazoline palladium(II) complexes *trans*-[**Pd**$Cl_2${N=C(R)ONC(H)$CH_2CH_2CMe_2$}$_2$].

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