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Pt^{II} versus Pd^{II}-assisted [2+3] cycloadditions of nitriles and nitron.**Synthesis of nitrile-derived arylamido platinum(II) and Δ^4 -1,2,4-oxadiazoline palladium(II) complexes****Jamal Lasri^{a,*}, Naser Eltaher Eltayeb^a, Matti Haukka^b, Bandar A. Babgi^a**^a*Department of Chemistry, Rabigh College of Science and Arts, P.O. Box 344, King Abdulaziz University, Jeddah, Saudi Arabia*^b*University of Jyväskylä, Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014, Finland*

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E-mail address: jlasri@kau.edu.sa (J. Lasri).**ABSTRACT**

The reactions of bis(organonitrile) platinum(II) complexes *trans*-[PtCl₂(N≡CR)₂] (R = C₆H₄(*p*-HC=O), CH₂C₆H₄(*p*-CH₃)) with pyrroline *N*-oxide ⁻O⁺N=CHCH₂CH₂CMe₂ afford arylamido platinum(II) complexes *trans*-[PtCl₂{(O=CR)N=CCH₂CH₂CMe₂NH}₂] (R = C₆H₄(*p*-HC=O) (**1**), CH₂C₆H₄(*p*-CH₃) (**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*-[PdCl₂(N≡CR)₂] with pyrroline *N*-oxide furnish Δ^4 -1,2,4-oxadiazoline palladium(II) complexes *trans*-[PdCl₂{N=C(R)ONC(H)CH₂CH₂CMe₂}₂] (R = C₆H₄(*p*-HC=O) (**3**), CH₂C₆H₄(*p*-CH₃) (**4**)) as the exclusive detected products. Compounds **1–4** have been characterized by IR, ¹H, ¹³C 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**

The 1,3-dipolar cycloaddition reactions of organonitriles with nitrones is one of the most important routes for the preparation of Δ^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 synthesize directly by pure organic chemistry [1]. The N–O bond cleavage of the Δ^4 -1,2,4-oxadiazoline ligands can be promoted by thermal heating to afford ketoimine palladium(II) complexes [5]. However, the Δ^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 $[\text{PtCl}_2(\text{RCN})_2]$ ($\text{R} = \text{CH}_2\text{Cl}$, $\text{CH}_2\text{CO}_2\text{Me}$) 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*- $[\text{PtCl}_2(\text{N}\equiv\text{CR})_2]$ with pyrroline *N*-oxide afford *trans*- $[\text{PtCl}_2\{(\text{O}=\text{CR})\text{N}=\text{CCH}_2\text{CH}_2\text{CMe}_2\text{NH}\}_2]$ complexes ($\text{R} = \text{C}_6\text{H}_4(p\text{-HC}=\text{O})$ (**1**), $\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3)$ (**2**)) as a result of the N–O bond cleavage of the oxadiazoline rings. In contrast, the reactions of *trans*- $[\text{PdCl}_2(\text{N}\equiv\text{CR})_2]$ with pyrroline *N*-oxide furnish *trans*- $[\text{PdCl}_2\{\text{N}=\text{C}(\text{R})\text{ONC}(\text{H})\text{CH}_2\text{CH}_2\text{CMe}_2\}_2]$ complexes ($\text{R} = \text{C}_6\text{H}_4(p\text{-HC}=\text{O})$ (**3**), $\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3)$ (**4**)) as the exclusive detected products.

2. Experimental section

2.1. General methods

The bis(*p*-cyanobenzaldehyde) platinum(II) and palladium(II) complexes *trans*- $[\text{MCl}_2(\text{N}\equiv\text{CC}_6\text{H}_4(p\text{-HC}=\text{O}))_2]$ ($\text{M} = \text{Pt}, \text{Pd}$) and bis(*p*-tolylacetonitrile) platinum(II) and palladium(II) complexes *trans*- $[\text{MCl}_2(\text{N}\equiv\text{CCH}_2\text{C}_6\text{H}_4(p\text{-CH}_3))_2]$ ($\text{M} = \text{Pt}, \text{Pd}$) were previously synthesized by one of us [2b,9]. Moreover, the Δ^4 -1,2,4-oxadiazoline palladium(II) complex (**3**) was also reported by one of us in our previous work [2b].

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} . ^1H 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*-[PtCl₂(N≡CR)₂] (*R* = C₆H₄(*p*-HC=O), CH₂C₆H₄(*p*-CH₃)) with pyrroline *N*-oxide $\cdot\text{O}^+\text{N}=\text{CHCH}_2\text{CH}_2\text{CMe}_2$

Pyrroline *N*-oxide (21.2 mg, 0.187 mmol) was added to a solution of *trans*-[PtCl₂(N≡CC₆H₄(*p*-HC=O))₂] (45.0 mg, 0.085 mmol) or *trans*-[PtCl₂(N≡CCH₂C₆H₄(*p*-CH₃))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*-[PtCl₂(N≡CC₆H₄(*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*-[PtCl₂{(O=CC₆H₄(*p*-HC=O))N=CCH₂CH₂CMe₂NH}₂] (**1**)

IR (cm^{-1}): 1699 $\nu(\text{NC}=\text{O})$, 1654 $\nu(\text{N}=\text{C})$, 3258 $\nu(\text{NH})$. ^1H NMR (CDCl_3), δ : 1.31 (s, 12H, CH₃), 1.74 (s, 4H, CH₂), 2.98 (s, 4H, CH₂), 8.02 (d, J_{HH} 8.1 Hz, 4H, CH_{aromatic}),

8.18 (d, J_{HH} 8.1 Hz, 4H, $\text{CH}_{\text{aromatic}}$), 10.13 (s, 2H, $\text{HC}=\text{O}$). ^{13}C NMR (CDCl_3), δ : 28.3 (CH_3), 128.8, 129.9, 137.1, 145.4 ($\text{C}_{\text{aromatic}}$), 174.5 ($\text{NC}=\text{O}$), 191.7 ($\text{HC}=\text{O}$). The other signals cannot be detected by ^{13}C NMR even after a long accumulation period. Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_4\text{Cl}_2\text{Pt}$ (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 $[\text{M}]^+$.

2.2.2. *Trans*-[PtCl₂{(O=CCH₂C₆H₄(*p*-CH₃))N=CCH₂CH₂CMe₂NH}₂]}] (2)

IR (cm^{-1}): 1669 $\nu(\text{NC}=\text{O})$, 1577 $\nu(\text{N}=\text{C})$, 3417 $\nu(\text{NH})$. ^1H NMR (CDCl_3), δ : 1.36 (s, 12H, CH_3), 1.99 (m, 4H, CH_2), 2.37 (m, 6H, CH_3), 4.00 (t, J_{HH} 7.4 Hz, 4H, CH_2), 5.09 (s, 4H, CH_2), 7.15-7.22 (m, 8H, $\text{CH}_{\text{aromatic}}$), 10.89 (bs, 2H, NH). ^{13}C NMR (CDCl_3), δ : 21.1 (CH_3), 28.7 (CH_3), 32.9 (CH_2), 47.2 (CH_2), 65.1 (C-NH), 129.1, 130.0, 131.9, 136.6 ($\text{C}_{\text{aromatic}}$), 173.6 ($\text{N}=\text{C}$), 184.6 ($\text{NC}=\text{O}$). Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{N}_4\text{O}_2\text{Cl}_2\text{Pt}$ (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 $[\text{M}]^+$.

2.3. Reaction of *trans*-[PdCl₂(N≡CCH₂C₆H₄(*p*-CH₃))₂] with pyrroline *N*-oxide $\text{O}^+\text{N}=\text{CHCH}_2\text{CH}_2\text{CMe}_2$

Pyrroline *N*-oxide (21.2 mg, 0.187 mmol) was added to a solution of *trans*-[PdCl₂(N≡CCH₂C₆H₄(*p*-CH₃))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*-[PdCl₂{N=C(CH₂C₆H₄(*p*-CH₃))ONC(H)CH₂CH₂CMe₂}₂]}] (4)

IR (cm^{-1}): 1659 $\nu(\text{C}=\text{N})$. ^1H NMR (CDCl_3), δ : 0.98 and 1.01 (two s, 6H, two CH_3), 1.07 and 1.09 (two s, 6H, two CH_3), 1.26-1.32 (m, 2H, CH_2), 1.55-1.70 (m, 6H, three CH_2), 2.29 and 2.31 (two s, 6H, two CH_3), 2.93-2.97 (m, 2H, CH_2), 4.21-4.27 (m, 2H, CH_2), 5.46 (t, J_{HH} 5.4 Hz, 2H, N-CH-N), 7.12-7.22 (m, 4H, $\text{CH}_{\text{aromatic}}$), 7.34-7.39 (m, 4H, $\text{CH}_{\text{aromatic}}$). ^{13}C NMR (CDCl_3), δ : 21.1, 22.2 and 27.2 (CH_3), 30.2, 33.5 and 33.9 (CH_2), 69.9 ($\text{Me}_2\text{C-N}$), 88.4 (N-CH-N), 127.8, 129.4, 129.7 and 137.3 ($\text{C}_{\text{aromatic}}$), 167.5 and

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)
λ (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)
α (°)	100.680(15)
β (°)	105.685(15)
γ (°)	103.623(14)
V (Å ³)	1106.5(11)
Z	1
ρ_{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 $RI = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

3. Results and discussion

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

The reaction of bis(*p*-cyanobenzaldehyde) platinum(II) complex *trans*-[PtCl₂(N≡CC₆H₄(*p*-HC=O))₂] with pyrroline *N*-oxide ⁻O⁺N=CHCH₂CH₂CMe₂, in CHCl₃ at room temperature for 2 h, affords *trans*-dichloridobis[(*Z*)-*p*-formyl-*N*-(5,5-dimethylpyrrolidin-2-ylidene)benzamide] platinum(II) complex *trans*-[PtCl₂{(O=CC₆H₄(*p*-HC=O))N=CCH₂CH₂CMe₂NH}₂] (**1**) as the exclusive detected product (Scheme 1, reaction *a*), instead of the expected Δ⁴-1,2,4-oxadiazoline platinum(II) complex *trans*-[PtCl₂{N=C(C₆H₄(*p*-HC=O))ONC(H)CH₂CH₂CMe₂}₂] which has never been detected by NMR spectroscopy (Scheme 1, reaction *b*). Complex **1** has been characterized by IR, ¹H, ¹³C NMR spectroscopy, elemental analysis, ESI⁺-MS, and also by single crystal X-ray diffraction analysis which shows that the Δ⁴-1,2,4-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 ν(NC=O) and ν(N=C) vibrations at 1699 and 1654 cm⁻¹, respectively, and ν(NH) at 3258 cm⁻¹. In the ¹³C NMR spectrum, the NC=O resonances are detected at δ 174.5 ppm and confirm the N–O ring cleavage.

Scheme 1

On the other hand, the reaction of bis(*p*-tolylacetonitrile) platinum(II) complex *trans*- $[\text{PtCl}_2(\text{N}\equiv\text{CCH}_2\text{C}_6\text{H}_4(p\text{-CH}_3))_2]$ 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*- $[\text{PtCl}_2\{(\text{O}=\text{CCH}_2\text{C}_6\text{H}_4(p\text{-CH}_3))\text{N}=\text{CCH}_2\text{CH}_2\text{CMe}_2\text{NH}\}_2]$ (**2**) as the exclusive detected product (Scheme 1, reaction *a*). Also in this case, the expected Δ^4 -1,2,4-oxadiazoline platinum(II) complex *trans*- $[\text{PtCl}_2\{\text{N}=\text{C}(\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3))\text{ONC}(\text{H})\text{CH}_2\text{CH}_2\text{CMe}_2\}_2]$ 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 Δ^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 $\nu(\text{NC}=\text{O})$ and $\nu(\text{N}=\text{C})$ vibrations at 1669 and 1577 cm^{-1} , respectively, and $\nu(\text{NH})$ at 3417 cm^{-1} . In the ^1H NMR spectrum, the proton NH resonance is detected at δ 10.9 ppm. In the ^{13}C NMR spectrum, the N=C and

NC=O resonances are detected at δ 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 TLP Figure of structure **1** is shown in Fig. 1. The key non-covalent intermolecular interactions involving the platinum complex were located by using a Hirshfeld surface analysis. The Hirshfeld 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 CH₂-group of the five-membered ring (C14) is acting as a weak H-bond donor for the chloride of CHCl₃ (contact **E** in Fig. 2). Simultaneously, the H-atom of the CHCl₃ 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.* CHCl₃, 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.

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

Fig. 2. Hirshfeld 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

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 CHCl₃ (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*-[PdCl₂(N≡CC₆H₄(*p*-HC=O))₂] afforded Δ^4 -1,2,4-oxadiazoline palladium(II) complex *trans*-[PdCl₂{N=C(C₆H₄(*p*-HC=O))ONC(H)CH₂CH₂CMe₂}₂] (**3**). Hence, the reaction of bis(*p*-tolylacetonitrile) palladium(II) complex *trans*-[PdCl₂(N≡CCH₂C₆H₄(*p*-CH₃))₂] with pyrroline *N*-oxide, in CHCl₃ at room temperature for 2 h, furnishes Δ^4 -1,2,4-oxadiazoline palladium(II) complex *trans*-[PdCl₂{N=C(CH₂C₆H₄(*p*-CH₃))ONC(H)CH₂CH₂CMe₂}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*-[PdCl₂{(O=CCH₂C₆H₄(*p*-

$(\text{CH}_3)_2\text{N}=\text{CCH}_2\text{CH}_2\text{CMe}_2\text{NH}\}_2]$ has never been detected by NMR spectroscopy (Scheme 1, reaction *b*).

Complex **4** has been characterized by IR, ^1H , ^{13}C NMR spectroscopy, elemental analysis and ESI⁺-MS which shows that the *trans* Δ^4 -1,2,4-oxadiazoline rings have been formed without further N–O bond cleavage. The IR spectrum of complex **4** showed strong $\nu(\text{N}=\text{C})$ vibration at 1659 cm^{-1} . In the ^1H NMR spectrum, the proton N-CH-N resonance is detected at δ 5.46 ppm. In the ^{13}C NMR spectrum, the $\text{C}(\text{O})=\text{N}$ resonances are detected at δ 167.5 and 167.6 ppm, and confirm the formation of the Δ^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 ($\Delta\delta \sim 0.11\text{ ppm}$) 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) $^-\text{O}^+\text{N}=\text{CHCH}_2\text{CH}_2\text{CMe}_2$ offers a more rigid conformation (*E*) than in the case of the acyclic ones $^-\text{O}^+\text{N}(\text{Me})=\text{C}(\text{H})(\text{Ar})$ preventing one of the nitrone sides from the reaction, thus promoting the selectivity [2b,6,16].

Scheme 2

4. Conclusions

The results of this work show that the facile Pt^{II} -assisted [2+3] cycloaddition reaction of cyclic nitronium (pyrrolidine N-oxide) with organonitrile RCN ligands ($\text{R} = \text{C}_6\text{H}_4(p\text{-HC=O})$, $\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3)$), 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*- $[\text{PtCl}_2\{(\text{O=CR})\text{N}=\text{CCH}_2\text{CH}_2\text{CMe}_2\text{NH}\}_2]$ complexes ($\text{R} = \text{C}_6\text{H}_4(p\text{-HC=O})$ (**1**), $\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3)$ (**2**)). However, the expected Δ^4 -1,2,4-oxadiazoline platinum(II) complexes *trans*- $[\text{PtCl}_2\{\text{N}=\text{C}(\text{R})\text{ONC}(\text{H})\text{CH}_2\text{CH}_2\text{CMe}_2\}_2]$ ($\text{R} = \text{C}_6\text{H}_4(p\text{-HC=O})$, $\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3)$) 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 Δ^4 -1,2,4-oxadiazoline palladium(II) complexes *trans*- $[\text{PdCl}_2\{\text{N}=\text{C}(\text{R})\text{ONC}(\text{H})\text{CH}_2\text{CH}_2\text{CMe}_2\}_2]$ ($\text{R} = \text{C}_6\text{H}_4(p\text{-HC=O})$ (**3**), $\text{CH}_2\text{C}_6\text{H}_4(p\text{-CH}_3)$ (**4**)) as the exclusive products. Hence the

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 nitron with nitriles, at room temperature, affords in all cases Δ^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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Graphical abstract

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Synopsis

The reactions of *trans*-[PtCl₂(N≡CR)₂] with pyrroline *N*-oxide afford arylamido platinum(II) complexes *trans*-[PtCl₂{(O=CR)N=CCH₂CH₂CMe₂NH}₂] via one-pot reaction involving spontaneous N–O bond cleavage. However, the reactions of *trans*-[PdCl₂(N≡CR)₂] with pyrroline *N*-oxide furnish Δ^4 -1,2,4-oxadiazoline palladium(II) complexes *trans*-[PdCl₂{N=C(R)ONC(H)CH₂CH₂CMe₂}₂].