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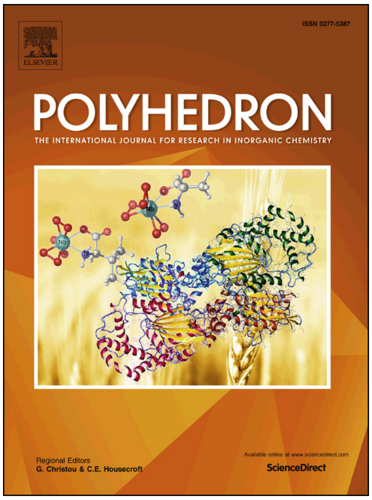

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Pt^{II} versus Pd^{II}-assisted [2+3] cycloadditions of nitriles and nitrone. Synthesis of nitrile-derived arylamido platinum(II) and Δ^4-1,2,4-oxadiazoline palladium(II) complexes

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ABSTRACT

The reactions of bis(organonitrile) platinum(II) complexes *trans*-[**Pt**$Cl_2(N{\equiv}CR)_2$] (R = C_6H_4(*p*-HC=O), $CH_2C_6H_4$(*p*-CH_3)) with pyrroline *N*-oxide $^-O^+N{=}CHCH_2CH_2CMe_2$ 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**$Cl_2(N{\equiv}CR)_2$] with pyrroline *N*-oxide furnish Δ^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, ^1H, ^{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

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 synthetize 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 $[PtCl_2(RCN)_2]$ (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*-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*-$CH_3$)$)_2$] (M = Pt, 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}. ^{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 =* $C_6H_4(p\text{-}HC{=}O)$, $CH_2C_6H_4(p\text{-}CH_3)$*) 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*-$[PtCl_2(N{\equiv}CC_6H_4(p\text{-}HC{=}O))_2]$ (45.0 mg, 0.085 mmol) or *trans*-$[PtCl_2(N{\equiv}CCH_2C_6H_4(p\text{-}CH_3))_2]$ (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*-$[PtCl_2(N{\equiv}CC_6H_4(p\text{-}HC{=}O))_2]$. 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-$[PtCl_2\{(O{=}CC_6H_4(p\text{-}HC{=}O))N{=}CCH_2CH_2CMe_2NH\}_2]$ *(**1**)*

IR (cm^{-1}): 1699 υ(NC=O), 1654 υ(N=C), 3258 υ(NH). ^{1}H NMR ($CDCl_3$), δ: 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, $CH_{aromatic}$), 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

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
μ(Kα) (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

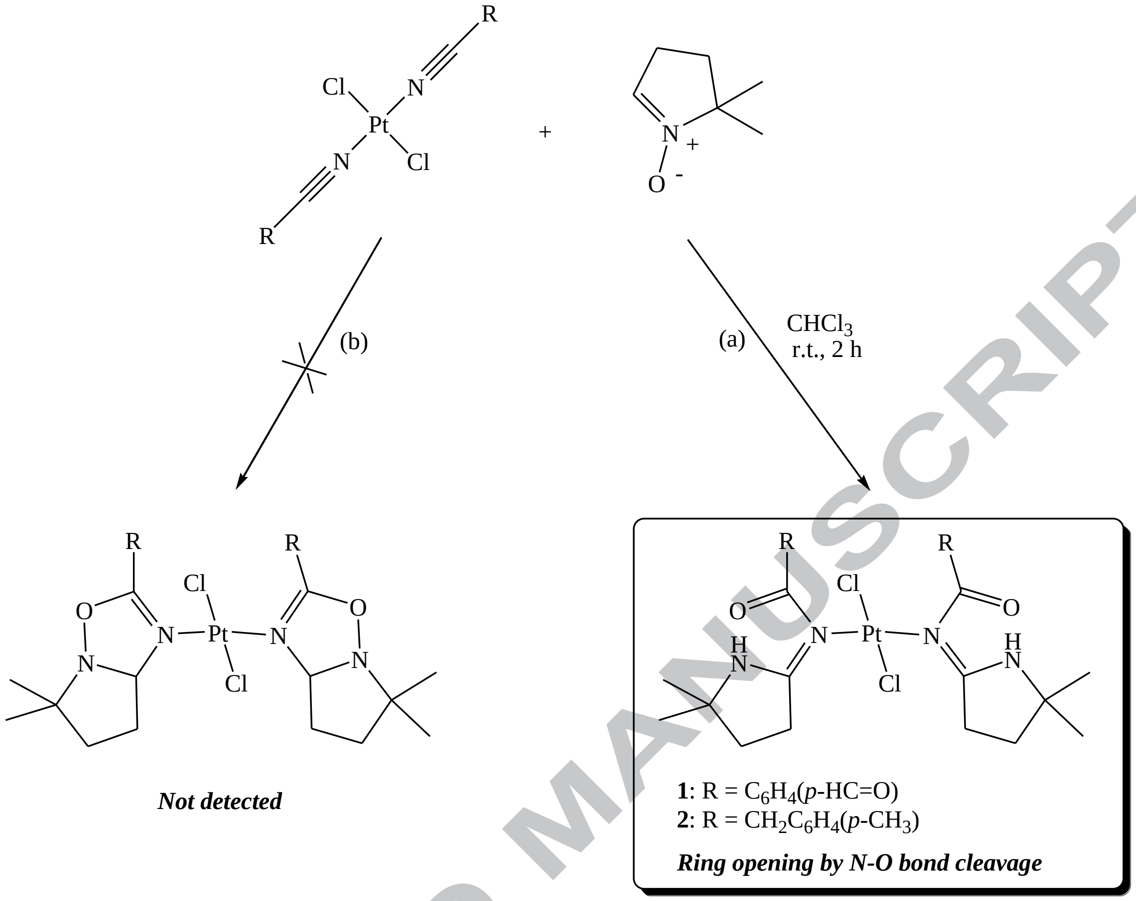
^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

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 Δ^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 Δ^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 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*-[$PtCl_2(N{\equiv}CCH_2C_6H_4(p\text{-}CH_3))_2$] 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 Δ^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 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 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 δ 10.9 ppm. In the ^{13}C NMR spectrum, the N=*C* and

N*C*=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 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.

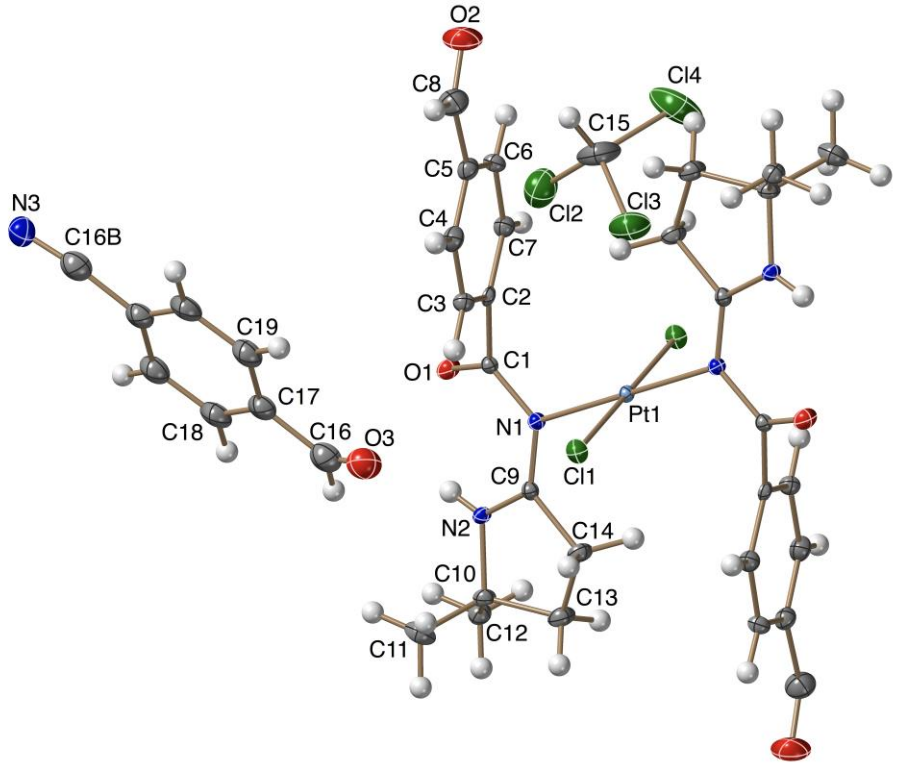


Fig. 1. The TELP drawing (50% probability level) of **1**. The halogen bond contact between the metal complex and $CHCl_3$ solvent molecule: Cl(1)···Cl(3): 3.295(2) Å, C(15)-Cl(3)···Cl(1): 166.82(11)°, Pt(1)-Cl(1)···Cl(3): 141.61(4)°.

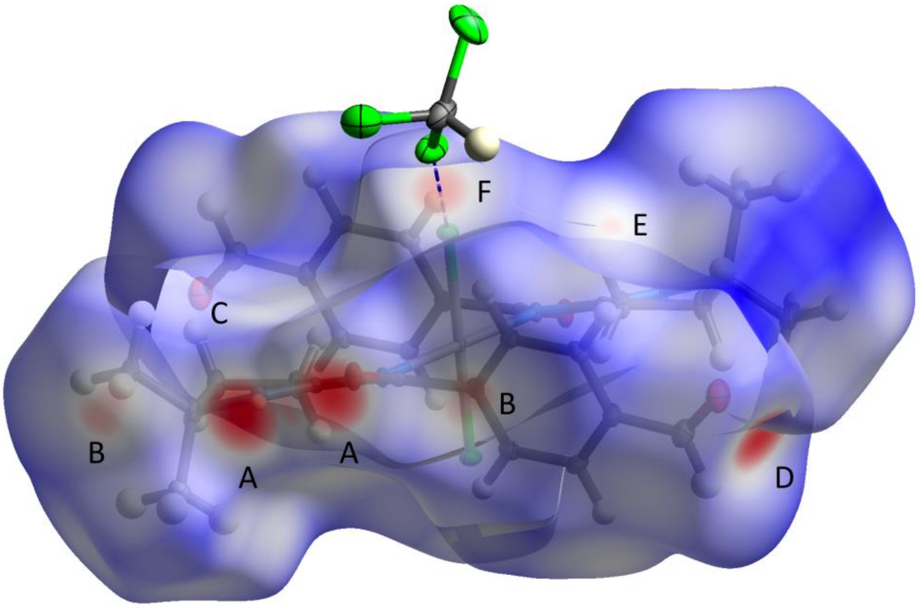


Fig. 2. Hirschfeld surface (d_{norm}) of **1**. The figure is generated by CrystalExplorer software [13]. Contacts: **A**: Hydrogen bond between N(2) and O(1), **B**: CH-π interaction

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.

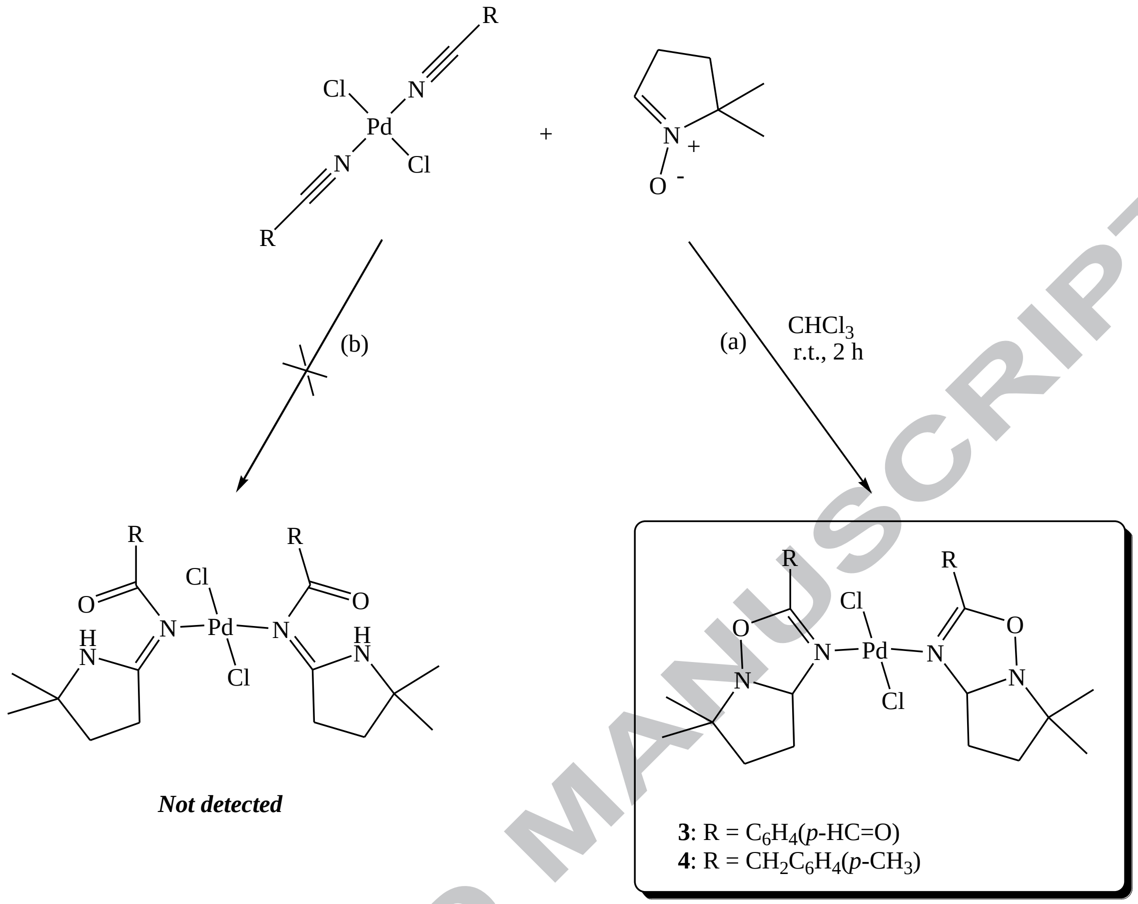
3.3. *Synthesis of palladium(II) complexes (**3**) and (**4**)*

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≡CC$_6$H$_4$(*p*-HC=O))$_2$] afforded Δ^4-1,2,4-oxadiazoline palladium(II) complex *trans*-[PdCl$_2${N=C(C$_6$H$_4$(*p*-HC=O))ONC(H)CH$_2$CH$_2$CMe$_2$}$_2$] (**3**). Hence, the reaction of bis(*p*-tolylacetonitrile) palladium(II) complex *trans*-[PdCl$_2$(N≡CCH$_2$C$_6$H$_4$(*p*-CH$_3$))$_2$] with pyrroline *N*-oxide, in CHCl$_3$ at room temperature for 2 h, furnishes Δ^4-1,2,4-oxadiazoline palladium(II) complex *trans*-[PdCl$_2${N=C(CH$_2$C$_6$H$_4$(*p*-CH$_3$))ONC(H)CH$_2$CH$_2$CMe$_2$}$_2$] (**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$_2$C$_6$H$_4$(*p*-

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* Δ^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 δ 5.46 ppm. In the ^{13}C NMR spectrum, the *C*(O)=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 ($\Delta\delta$ ~ 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].



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 = $C_6H_4(p\text{-}HC{=}O)$, $CH_2C_6H_4(p\text{-}CH_3)$), 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*-[**Pt**$Cl_2\{(O{=}CR)N{=}CCH_2CH_2CMe_2NH\}_2$] complexes (R = $C_6H_4(p\text{-}HC{=}O)$ (**1**), $CH_2C_6H_4(p\text{-}CH_3)$ (**2**)). However, the expected Δ^4-1,2,4-oxadiazoline platinum(II) complexes *trans*-[**Pt**$Cl_2\{N{=}C(R)ONC(H)CH_2CH_2CMe_2\}_2$] (R = $C_6H_4(p\text{-}HC{=}O)$, $CH_2C_6H_4(p\text{-}CH_3)$) 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*-[**Pd**$Cl_2\{N{=}C(R)ONC(H)CH_2CH_2CMe_2\}_2$] (R = $C_6H_4(p\text{-}HC{=}O)$ (**3**), $CH_2C_6H_4(p\text{-}CH_3)$ (**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 nitrone 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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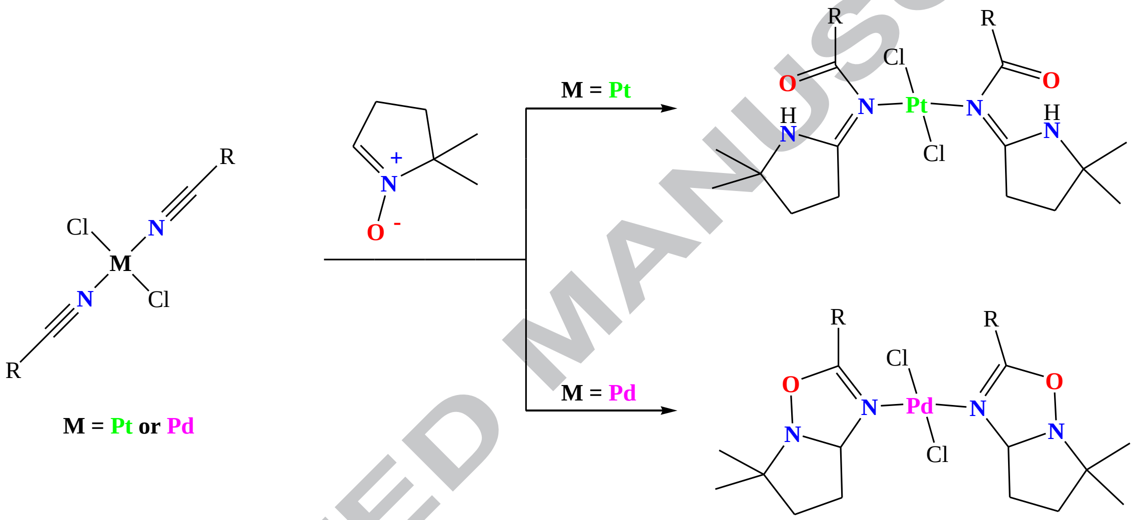
Graphical abstract



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Synopsis

The reactions of *trans*-[**Pt**$Cl_2(N{\equiv}CR)_2$] with pyrroline *N*-oxide afford arylamido platinum(II) complexes *trans*-[**Pt**$Cl_2\{(O{=}CR)N{=}CCH_2CH_2CMe_2NH\}_2$] *via* one-pot reaction involving spontaneous N–O bond cleavage. However, the reactions of *trans*-[**Pd**$Cl_2(N{\equiv}CR)_2$] with pyrroline *N*-oxide furnish Δ^4-1,2,4-oxadiazoline palladium(II) complexes *trans*-[**Pd**$Cl_2\{N{=}C(R)ONC(H)CH_2CH_2CMe_2\}_2$].