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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

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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

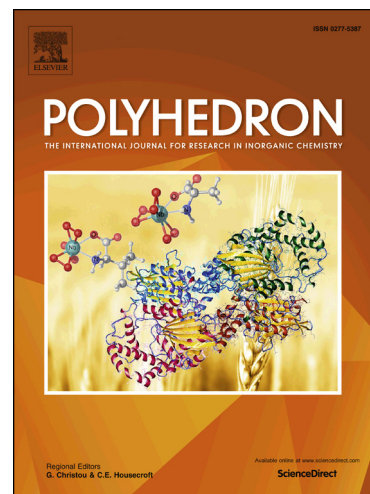**Jamal Lasri[a],*, Bruno Pedras,[b] Matti Haukka[c] and Mário N. Berberan-Santos[b]**

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ABSTRACT

Treatment of *trans*-[PtCl$_2$(NCR)$_2$] **1** (R = Me (**1a**), Et (**1b**), *o*-ClC$_6$H$_4$ (**1c**), *p*-ClC$_6$H$_4$ (**1d**), *p*-(HC=O)C$_6$H$_4$ (**1e**), *p*-O$_2$NC$_6$H$_4$CH$_2$ (**1f**)) with 1,3-diiminoisoindoline HN=$\underline{C}$C$_6$H$_4$C($\underline{N}$H)=NH **2** gives access to the corresponding (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes [PtCl{$\underline{N}$H=C(R)N=C(C$_6$H$_4$)$\underline{N}$C=NC(R)=$\underline{N}$H}] **3a-f**, in good yields (65–70 %). The reaction of *trans*-[PdCl$_2$(NCMe)$_2$] **4a** with **2** furnishes (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pd(II) complex [PdCl{$\underline{N}$H=C(Me)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Me)=$\underline{N}$H}] **5a**, in good yield (65%). However, the reaction of *trans*-[PdCl$_2$(NCR)$_2$] **4** (R = Ph (**4b**), *p*-MeC$_6$H$_4$CH$_2$ (**4c**), *p*-(HC=O)C$_6$H$_4$ (**4d**), *p*-O$_2$NC$_6$H$_4$CH$_2$ (**4e**)) with **2** gives a number of unidentified products. The compounds **3a-f** and **5a** were characterized by IR, ^{1}H, ^{13}C and DEPT-135 NMR spectroscopies, elemental analyses and, in the case of the Pt(II) complex [PtCl{$\underline{N}$H=C(Me)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Me)=$\underline{N}$H}] **3a**, also by X-ray diffraction analysis. Compounds **3a** and **3b** were also characterized by UV-vis absorption and luminescence emission spectroscopies. Emission quantum yields of *ca.* 3×10^{-3} were obtained in dichloromethane solution, and luminescence lifetimes are in the order of the tens of nanoseconds. Both compounds also exhibited luminescence in solid state (polystyrene matrix), with luminescence lifetimes in the order of hundreds of nanoseconds.

Keywords: Metal-assisted additions; Nitriles; 1,3-Diiminoisoindoline; Pentaazanonatetraene complexes; Luminescence.

1.   Introduction

Several methods to prepare coordination compounds by nucleophilic additions to nitrile ligands have been developed during the last two decades [1]. Various types of nucleophiles [2,3] or 1,3-dipoles [4] have been used for the preparation of compounds containing C–N and/or C–O bonds. 1,3-Diiminoisoindoline has been used for the synthesis of pthalocyanines [5] and hemiporphyrazine [6], which have a wide range of industrial applications. The iminoisoindoline-1-one, bearing a nucleophilic sp^2-imino group, has been used as a nucleophile in reaction with various metal-bound isonitriles and nitriles to furnish iminocarbene or triazapentadienato complexes, respectively [7]. However, 1,3-diiminoisoindoline contains two sp^2-nitrogen centres which can use both imine moieties for additions to metal-coordinated nitriles, thus furnishing symmetrical triazapentadienate complexes. In contrast to β-diimines, ligands such as triazapentadienes have one extra N donor site, and DFT [8] show that they have a greater capacity of coordination to metal ions than β-diimines. Nevertheless, the coordination chemistry of triazapendiene species is less reported, due to the instability of triazapentadiene complexes, particularly the unsubstituted ones [9]. A single-pot synthesis with electron-deficient nitriles has been used to synthetize triazapentadiene complexes [10]. Ni(II)-complexes bearing imidoylamidine ligands have been prepared using oximes and nitriles in the presence of Ni(II) ions [11], and this methodology has been used to synthetize a variety of (1,3,5-triazapentadienato)Pd(II) complexes [12]. Recently, we have also reported the synthesis of (alkoxy-1,3,5-triazapentadienato)Cu(II) complexes using a template synthesis [13].

On the other hand, Pt(II)-based imidoylamidinate compounds are emissive both in solid state and in solution, at room temperature. UV-visible and luminescence spectroscopies indicate that the lowest excited state of these complexes is ^{3}MLCT or ^{3}IL with significant MLCT character, with emission lifetimes of a few µs [14].

In continuation of our research program on the additions to metal-bound nitriles [15], we decided to extend the addition of a sp^2-nitrogen nucleophile, 1,3-diiminoisoindoline HN=$\underline{C}$C$_6$H$_4$C($\underline{N}$H)=NH **2**, i) to various Pt(II)-bound nitriles *trans*-[PtCl$_2$(NCR)$_2$] **1** (R = Me (**1a**), Et (**1b**), *o*-ClC$_6$H$_4$ (**1c**), *p*-ClC$_6$H$_4$ (**1d**), *p*-(HC=O)C$_6$H$_4$ (**1e**), *p*-O$_2$NC$_6$H$_4$CH$_2$ (**1f**)); and ii) to another type of metal complex such as Pd(II)-bound acetonitrile *trans*-[PdCl$_2$(NCMe)$_2$] **4a**; and also iii) to investigate the UV-vis absorption and the luminescence emission spectra of some of those complexes. We have thus observed the formation of (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) and Pd(II) complexes, **3a-f** and **5a**, respectively. The photophysical characterization of compounds **3a** and **3b** permitted the assessment of

parameters which, by correlation with other Pt(II) emissive complexes [14], enabled further insight into their electronic structure, namely in terms of optical transitions.

2. Experimental section

2.1. General methods

^{1}H, ^{13}C and DEPT-135 NMR spectra (in CDCl$_3$ or DMSO-d_6) were measured on Bruker Avance III HD 600 MHz (Ascend™ Magnet) spectrometer at ambient temperature. ^{1}H, ^{13}C and DEPT-135 chemical shifts (δ) are expressed in ppm relative to TMS. Infrared spectra (400-4000 cm^{-1}) were recorded on an Alpha Bruker FT-IR instrument in KBr pellets. C, H and N elemental analyses were carried out by the Microanalytical Service of the King Abdulaziz University.

The solvents used for photophysical characterization were all of spectroscopic grade. Dichloromethane (99.5% for spectroscopy, Acros Organics), chloroform ($\geq$ 99.8% ACS spectrometric grade, Sigma-Aldrich), ethanol (95%, UV HPLC spectroscopic, Sigma-Aldrich). Deionized water was obtained from a Millipore system Milli-Q $\geq$ 18 MΩ cm. Polystyrene beads (average M$_w$ 35000, Sigma-Aldrich) was used to prepare solid films of compounds **3a** and **3b**, by dissolving 1 mg of the respective compound in a solution of *ca.* 80 mg of polystyrene in 1 mL chloroform, which was subsequently deposited over a quartz plate, allowing the solvent to evaporate. Luminescence quantum yields were calculated by using Ru(bpy)$_3$ as reference quantum yield standard for compounds **3a** and **3b**. The electronic absorption spectra were recorded using a Jasco V-660 spectrophotometer. Fluorescence measurements were carried out in a Horiba-Jobin Yvon Fluorolog-3 spectrofluorimeter. All spectra were recorded with samples in 1 cm optical path length quartz cells, except for the solid films, where the film was placed directly in the optical path, in a 45° angle between the excitation source and the detector. Luminescence lifetime measurements were performed using the single-photon timing method with laser excitation and microchannel plate detection, with the set-up already described [16]. Excitation wavelength used was 335 nm for solution and 304 nm for solid state and the emission wavelength was 605 nm. The timescale was 438.2 ps/channel for solution measurements, 679.2 ps/channel for solid state **3a** and 786.7 ps/channel for solid state **3b**.

2.2. Preparation of the nitrile Pt(II) complexes trans-[PtCl$_2$(NCR)$_2$] **1** (R = Me (**1a**), Et (**1b**), o-ClC$_6$H$_4$ (**1c**), p-ClC$_6$H$_4$ (**1d**), p-(HC=O)C$_6$H$_4$ (**1e**), p-O$_2$NC$_6$H$_4$CH$_2$ (**1f**)) and their reactions with 1,3-diiminoisoindoline **2**

3

2.2.1. Reaction of PtCl$_2$ with liquid nitriles

PtCl$_2$ (200 mg, 0.752 mmol) was added at room temperature to acetonitrile or propionitrile (5 mL), and the mixture was heated under stirring at 70 °C for 8 h. During the course of the reaction, the green gray PtCl$_2$ powder dissolved, forming a homogeneous light yellow solution. The reaction mixture was then dried *in vacuo*, washed with three 5 mL portions of diethyl ether and dried under air to give *trans*-[PtCl$_2$(NCMe)$_2$] **1a** or *trans*-[PtCl$_2$(NCEt)$_2$] **1b**, respectively, in excellent yields (*ca.* 90%).

2.2.2. Reaction of PtCl$_2$ with solid nitriles

PtCl$_2$ (200 mg, 0.752 mmol) was added at room temperature to *o*-chlorobenzonitrile (1034 mg, 7.52 mmol), *p*-chlorobenzonitrile (1034 mg, 7.52 mmol), *p*-cyanobenzaldehyde (986 mg, 7.52 mmol) or *p*-nitrophenylacetonitrile (1218 mg, 7.52 mmol), and the mixture was heated at the melting point of each nitrile (46, 93, 102 or 115 °C, respectively) in a sealed glass vial for 12 h. Also in this case, during the course of the reaction, the green gray PtCl$_2$ powder dissolved in the melted nitrile, forming a homogeneous light yellow solution. The excess of nitrile was then removed by washing the reaction mixture with three 10 mL portions of diethyl ether or chloroform (depending on the solubility of the nitrile used) and dried under air to give *trans*-[PtCl$_2$(NC(*o*-ClC$_6$H$_4$))$_2$] **1c**, *trans*-[PtCl$_2$(NC(*p*-ClC$_6$H$_4$))$_2$] **1d**, *trans*-[PtCl$_2$(NC(*p*-(HC=O)C$_6$H$_4$))$_2$] **1e** or *trans*-[PtCl$_2$(NC(*p*-O$_2$NC$_6$H$_4$CH$_2$))$_2$] **1f**, respectively, in excellent yields (*ca.* 87%).

To confirm the formation of those Pt(II) complexes, the new compounds *e.g.* **1c** and **1e** were characterized by ^{1}H, ^{13}C and DEPT-135 NMR spectroscopy, then the NMR data were compared with their respective starting materials (*o*-chlorobenzonitrile and *p*-cyanobenzaldehyde).

o-Chlorobenzonitrile N≡C(*o*-ClC$_6$H$_4$)
^{1}H NMR (CDCl$_3$), δ: 7.40 (t, J_{HH} 7.5 Hz, 1H, C*H*$_{aromatic}$), 7.53-7.58 (m, 2H, C*H*$_{aromatic}$), 7.69 (d, J_{HH} 7.7 Hz, 1H, C*H*$_{aromatic}$). ^{13}C NMR (CDCl$_3$), δ: 113.4 (*C*≡N), 115.9 (Cl-*C*$_{aromatic}$), 127.1, 130.1, 133.9, 134.0, 136.9 (C$_{aromatic}$). DEPT-135 NMR (CDCl$_3$), δ: 127.1, 130.1, 133.9, 134.0 (*C*H$_{aromatic}$).

Trans-[PtCl$_2$(NC(*o*-ClC$_6$H$_4$))$_2$] (**1c**)
Yield: 87%. ^{1}H NMR (CDCl$_3$), δ: 7.49 (t, J_{HH} 7.7 Hz, 2H, C*H*$_{aromatic}$), 7.60 (d, J_{HH} 8.2 Hz, 2H, C*H*$_{aromatic}$), 7.70 (t, J_{HH} 7.7 Hz, 2H, C*H*$_{aromatic}$), 7.80 (d, J_{HH} 7.8 Hz, 2H, C*H*$_{aromatic}$). ^{13}C NMR (CDCl$_3$), δ:

110.5 (Cl-$C_{aromatic}$), 114.1 ($C\equiv N$), 127.4, 130.5, 135.5, 136.3, 138.9 ($C_{aromatic}$). DEPT-135 NMR (CDCl$_3$), δ: 127.4, 130.5, 135.5, 136.3 ($CH_{aromatic}$).

p-Cyanobenzaldehyde $N\equiv C(p\text{-}(HC=O)C_6H_4)$

^{1}H NMR (CDCl$_3$), δ: 7.86 (d, J_{HH} 8.3 Hz, 2H, C$H_{aromatic}$), 8.00 (d, J_{HH} 8.3 Hz, 2H, C$H_{aromatic}$), 10.10 (s, 1H, HC=O). ^{13}C NMR (CDCl$_3$), δ: 117.6 and 117.7 ($C\equiv N$), 129.9, 132.9, 138.7 (C$_{aromatic}$), 190.6 (HC=O). DEPT-135 NMR (CDCl$_3$), δ: 129.9, 132.9 (C$H_{aromatic}$), 190.6 (HC=O).

Trans-[PtCl$_2$(NC(*p*-(HC=O)C$_6$H$_4$))$_2$] (**1e**)

Yield: 85%. ^{1}H NMR (CDCl$_3$), δ: 8.04 (d, J_{HH} 8.4 Hz, 4H, C$H_{aromatic}$), 8.10 (d, J_{HH} 8.4 Hz, 4H, C$H_{aromatic}$), 10.16 (s, 2H, HC=O). ^{13}C NMR (CDCl$_3$), δ: 113.9 and 115.8 ($C\equiv N$), 129.9, 134.6, 140.3 (C$_{aromatic}$), 190.0 (HC=O). DEPT-135 NMR (CDCl$_3$), δ: 129.9, 134.6 (C$H_{aromatic}$), 190.0 (HC=O).

2.2.3. Reactions of the nitrile Pt(II) complexes trans-[PtCl$_2$(NCR)$_2$] 1 (R = Me (1a), Et (1b), o-ClC$_6$H$_4$ (1c), p-ClC$_6$H$_4$ (1d), p-(HC=O)C$_6$H$_4$ (1e), p-O$_2$NC$_6$H$_4$CH$_2$ (1f)) with 1,3-diiminoisoindoline 2

To a solution of **1a**, **1b**, **1c**, **1d**, **1e** or **1f** (0.532 mmol) in chloroform (5 mL) was added at room temperature to 1,3-diiminoisoindoline **2** (77.2 mg, 0.532 mmol), and the mixture was refluxed for 2 h whereupon the solvent was removed *in vacuo*. The crude residue was purified by column chromatography on silica (chloroform as the eluent), followed by evaporation of the solvent *in vacuo* to give the final **3a**, **3b**, **3c**, **3d**, **3e** or **3f** products, respectively.

[PtCl{$\underline{N}$H=C(Me)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Me)=$\underline{N}$H}] (**3a**)

Yield: 67%. IR (cm^{-1}): 3441 (NH), 1628 (C=N). ^{1}H NMR (CDCl$_3$), δ: 2.55 (s, 6H, CH_3), 7.75 (dd, J_{HH} 3.0 and 5.5 Hz, 2H, C$H_{aromatic}$), 8.24 (dd, J_{HH} 3.0 and 5.5 Hz, 2H, C$H_{aromatic}$), 9.80 (s, br, 2H, NH). ^{13}C NMR (CDCl$_3$), δ: 28.8 (CH_3), 123.2, 132.2, 137.9 (C$_{aromatic}$), 153.1, 159.8 (C=N). DEPT-135 NMR (CDCl$_3$), δ: 28.8 (CH_3), 123.2, 132.2 (C$H_{aromatic}$). Anal. Calcd for C$_{12}$H$_{12}$N$_5$ClPt (456.79): C, 31.55; H, 2.65; N, 15.33. Found: C, 31.67; H, 2.74; N, 15.28.

[PtCl{$\underline{N}$H=C(Et)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Et)=$\underline{N}$H}] (**3b**) [15]

Yield: 65%. IR (cm^{-1}): 3443 (NH), 1615 (C=N). ^{1}H NMR (CDCl$_3$), δ: 1.47 (t, J_{HH} 7.5 Hz, 6H, CH_3CH$_2$), 2.82 (q, J_{HH} 7.5 Hz, 4H, CH$_3$CH_2), 7.75 (dd, J_{HH} 3.0 and 5.4 Hz, 2H, C$H_{aromatic}$), 8.26 (dd, J_{HH} 3.0 and 5.4 Hz, 2H, C$H_{aromatic}$), 9.77 (s, br, 2H, NH). ^{13}C NMR (CDCl$_3$), δ: 11.0 (CH_3), 35.1 (CH_2), 123.2,

5

132.1, 137.9 (C$_{aromatic}$), 153.2 and 163.8 (*C*=N). DEPT-135 NMR (CDCl$_3$), *δ*: 11.0 (*C*H$_3$), 35.1 (*C*H$_2$), 123.2, 132.1 (*C*H$_{aromatic}$). Calcd for C$_{14}$H$_{16}$N$_5$ClPt (484.84): C, 34.68; H, 3.33; N, 14.44. Found: C, 34.74; H, 3.25; N, 14.33.

[PtCl{NH=C(*o*-ClC$_6$H$_4$)N=C(C$_6$H$_4$)NC=NC(*o*-ClC$_6$H$_4$)=NH}] (**3c**)

Yield: 68%. IR (cm^{-1}): 2926 (NH), 1678 (C=N). ^{1}H NMR (CDCl$_3$), *δ*: 7.48 (t, *J*$_{HH}$ 7.7 Hz, 2H, C*H*$_{aromatic}$), 7.53-7.61 (m, 4H, C*H*$_{aromatic}$), 7.70 (t, *J*$_{HH}$ 7.7 Hz, 2H, C*H*$_{aromatic}$), 7.80 (m, 2H, C*H*$_{aromatic}$), 8.04 (d, *J*$_{HH}$ 7.6 Hz, 1H, C*H*$_{aromatic}$), 8.36 (dd, *J*$_{HH}$ 3.0 and 5.5 Hz, 1H, C*H*$_{aromatic}$), 10.80 (s, br, 2H, N*H*). ^{13}C NMR (CDCl$_3$), *δ*: 110.5 (Cl-*C*$_{aromatic}$), 123.6, 127.3, 127.4, 130.5, 130.7, 131.0, 131.6, 132.4, 135.5, 136.3, 138.9 (C$_{aromatic}$), 153.7 and 155.9 (*C*=N). DEPT-135 NMR (CDCl$_3$), *δ*: 123.6, 127.3, 127.4, 130.5, 130.7, 131.0, 131.6, 132.4, 135.5, 136.3 (*C*H$_{aromatic}$). Anal. Calcd for C$_{22}$H$_{14}$N$_5$Cl$_3$Pt (649.82): C, 40.66; H, 2.17; N, 10.78. Found: C, 40.78; H, 2.55; N, 10.21.

[PtCl{NH=C(*p*-ClC$_6$H$_4$)N=C(C$_6$H$_4$)NC=NC(*p*-ClC$_6$H$_4$)=NH}] (**3d**)

Yield: 69%. IR (cm^{-1}): 3196 (NH), 1677 (C=N). ^{1}H NMR (CDCl$_3$), *δ*: 7.58 (d, *J*$_{HH}$ 8.6 Hz, 6H, C*H*$_{aromatic}$), 7.77 (d, *J*$_{HH}$ 8.6 Hz, 4H, C*H*$_{aromatic}$), 8.24 (d, *J*$_{HH}$ 8.6 Hz, 1H, C*H*$_{aromatic}$), 8.36 (dd, *J*$_{HH}$ 3.0 and 5.4 Hz, 1H, C*H*$_{aromatic}$), 10.36 (s, br, 2H, N*H*). ^{13}C NMR (CDCl$_3$), *δ*: 107.2 (Cl-*C*$_{aromatic}$), 123.5, 128.8, 129.5, 130.2, 132.4, 134.9, 142.7 (C$_{aromatic}$), 153.9 and 155.3 (*C*=N). DEPT-135 NMR (CDCl$_3$), *δ*: 123.5, 128.8, 129.5, 130.2, 132.4, 134.9 (*C*H$_{aromatic}$). Anal. Calcd for C$_{22}$H$_{14}$N$_5$Cl$_3$Pt (649.82): C, 40.66; H, 2.17; N, 10.78. Found: C, 40.53; H, 2.45; N, 10.61.

[PtCl{NH=C(*p*-(HC=O)C$_6$H$_4$)N=C(C$_6$H$_4$)NC=NC(*p*-(HC=O)C$_6$H$_4$)=NH}] (**3e**)

Yield: 67%. IR (cm^{-1}): 3424 (NH), 1607 (C=N), 1702 (C=O). ^{1}H NMR (CDCl$_3$), *δ*: 7.87 (dd, *J*$_{HH}$ 3.0 and 5.4 Hz, 2H, C*H*$_{aromatic}$), 8.11 (d, *J*$_{HH}$ 8.4 Hz, 4H, C*H*$_{aromatic}$), 8.44 (dd, *J*$_{HH}$ 3.0 and 5.4 Hz, 2H, C*H*$_{aromatic}$), 8.48 (d, *J*$_{HH}$ 8.4 Hz, 4H, C*H*$_{aromatic}$), 10.20 (s, 2H, *H*C=O), 10.61 (s, br, 2H, N*H*). ^{13}C NMR (CDCl$_3$), *δ*: 123.7, 128.2, 129.9, 130.4, 132.7, 132.9, 137.9, 138.1, 141.7 (C$_{aromatic}$), 154.2 and 155.3 (*C*=N), 191.5 (H*C*=O). DEPT-135 NMR (CDCl$_3$), *δ*: 123.7, 128.2, 129.9, 130.4, 132.7, 132.9 (*C*H$_{aromatic}$), 191.5 (H*C*=O). Anal. Calcd for C$_{24}$H$_{16}$N$_5$ClO$_2$Pt (636.95): C, 45.26; H, 2.53; N, 11.00. Found: C, 45.37; H, 2.19; N, 11.25.

[PtCl{NH=C(*p*-O$_2$NC$_6$H$_4$CH$_2$)N=C(C$_6$H$_4$)NC=NC(*p*-O$_2$NC$_6$H$_4$CH$_2$)=NH}] (**3f**)

Yield: 64%. IR (cm^{-1}): 3270 (NH), 1605 (C=N). ^{1}H NMR (CDCl$_3$), *δ*: 4.22 (s, 4H, C*H*$_2$) 7.60 (d, *J*$_{HH}$ 8.8 Hz, 4H, C*H*$_{aromatic}$), 7.77 (dd, *J*$_{HH}$ 3.1 and 5.4 Hz, 2H, C*H*$_{aromatic}$), 8.18 (dd, *J*$_{HH}$ 3.1 and 5.4 Hz, 2H,

C$H_{aromatic}$), 8.25 (d, J_{HH} 8.8 Hz, 4H, C$H_{aromatic}$), 9.96 (s, br, 2H, NH). ^{13}C NMR (CDCl$_3$), δ: 47.7 (CH_2), 123.5, 124.1, 124.4, 128.9, 130.4, 132.6, 134.3, 137.6, 141.7, 147.5 (C$_{aromatic}$), 153.9 and 159.6 (*C*=N). DEPT-135 NMR (CDCl$_3$), δ: 47.7 (CH_2), 123.5, 124.1, 124.4, 128.9, 130.4, 132.6, 134.3 (C$H_{aromatic}$). Anal. Calcd for C$_{24}$H$_{18}$N$_7$ClO$_4$Pt (698.98): C, 41.24; H, 2.60; N, 14.03. Found: C, 41.55; H, 2.73; N, 14.15.

*2.3. Preparation of the nitrile Pd(II) complexes trans-[PdCl$_2$(NCR)$_2$] **4** (R = Me (**4a**), Ph (**4b**), p-MeC$_6$H$_4$CH$_2$ (**4c**), p-(HC=O)C$_6$H$_4$ (**4d**), p-O$_2$NC$_6$H$_4$CH$_2$ (**4e**)) and their reactions with 1,3-diiminoisoindoline **2***

2.3.1. Reaction of PdCl$_2$ with liquid nitriles

PdCl$_2$ (200 mg, 1.127 mmol) was added at room temperature to acetonitrile, benzonitrile or *p*-tolylacetonitrile (5 mL), and the mixture was heated under stirring at 70 °C for 8 h. During the course of the reaction, the brown PdCl$_2$ powder dissolved, forming a homogeneous light yellow solution. The reaction mixture was then dried *in vacuo*, washed with three 5 mL portions of diethyl ether and dried under air to give yellow solid compounds *trans*-[PdCl$_2$(NCMe)$_2$] **4a**, *trans*-[PdCl$_2$(NCPh)$_2$] **4b** or *trans*-[PdCl$_2$(NC(*p*-MeC$_6$H$_4$CH$_2$))$_2$] **4c**, respectively.
The Pd(II) complexes **4a**, **4b** and **4c** were used without further characterization.

2.3.2. Reaction of PdCl$_2$ with solid nitriles

PdCl$_2$ (200 mg, 1.127 mmol) was added at room temperature to *p*-cyanobenzaldehyde (1477 mg, 11.27 mmol) or *p*-nitrophenylacetonitrile (1825 mg, 11.27 mmol), and the mixture was heated at the melting point of each nitrile (102 or 115 °C, respectively) in a sealed glass vial for 12 h. Also in this case, during the course of the reaction, the brown PdCl$_2$ powder dissolved in the melted nitrile, forming a homogeneous light yellow solution. The excess of nitrile was then removed by washing the reaction mixture with three 10 mL portions of chloroform and dried under air to give yellow solid compounds *trans*-[PdCl$_2$(NC(*p*-(HC=O)C$_6$H$_4$))$_2$] **4d** or *trans*-[PdCl$_2$(NC(*p*-O$_2$NC$_6$H$_4$CH$_2$))$_2$] **4e**, respectively.
The Pd(II) complexes **4d** and **4e** were used without further characterization.

*2.3.3. Reactions of the nitrile Pd(II) complexes trans-[PdCl$_2$(NCR)$_2$] **4** (R = Me (**4a**), Ph (**4b**), p-MeC$_6$H$_4$CH$_2$ (**4c**)) with 1,3-diiminoisoindoline **2***

7

A solution of **4a**, **4b** or **4c** (0.532 mmol) in acetonitrile, benzonitrile or *p*-tolylacetonitrile (5 mL), respectively, was added at room temperature to 1,3-diiminoisoindoline **2** (77.2 mg, 0.532 mmol), and the mixture was refluxed for 2 h whereupon the solvent was removed *in vacuo*. The crude residue was washed with three 5 mL portions of diethyl ether and dried under air.

After a careful IR and NMR analyses of each compound, it was observed that only the Pd(II) complex [PdCl{$\underline{N}$H=C(Me)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Me)=$\underline{N}$H}] (**5a**) was formed.

[PdCl{$\underline{N}$H=C(Me)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Me)=$\underline{N}$H}] (**5a**)

Yield: 65%. IR (cm^{-1}): 3440 (NH), 1639 (C=N). ^{1}H NMR (DMSO-d_6), δ: 2.57 (s, 6H, C*H$_3$*), 7.75 (m, 2H, C*H*$_{aromatic}$), 8.20 (m, 2H, C*H*$_{aromatic}$), 10.20 (s, br, 1H, N*H*), 10.33 (s, br, 1H, N*H*). ^{13}C NMR (DMSO-d_6), δ: 27.1 (*C*H$_3$), 123.3, 124.1, 133.8, 133.9, 134.8, 137.9 (*C*$_{aromatic}$), 156.3, 164.8 (*C*=N). Anal. Calcd for C$_{12}$H$_{12}$N$_5$ClPd (368.13): C, 39.15; H, 3.29; N, 19.02. Found: C, 39.46; H, 3.53; N, 19.27.

2.3.4.   Reactions of the nitrile Pd(II) complexes trans-[PdCl$_2$(NCR)$_2$] 4 (R = p-(HC=O)C$_6$H$_4$ (4d), p-O$_2$NC$_6$H$_4$CH$_2$ (4e)) with 1,3-diiminoisoindoline 2

A solution of **4d** or **4e** (0.532 mmol) in acetone (5 mL) was added at room temperature to 1,3-diiminoisoindoline **2** (77.2 mg, 0.532 mmol), and the mixture was refluxed for 2 h whereupon the solvent was removed *in vacuo*. The crude residue was washed with three 5 mL portions of diethyl ether and dried under air.

After a careful IR and NMR analyses of each reaction product, it was observed the absence of the products of the addition of 1,3-diiminoisoindoline to nitrile group (N≡*C*), the resulting mixtures contain a number of unidentified products. Additionally, the reaction of **4e** with **2** affords also *p*-nitrophenylacetonitrile (resulting from the decomposition of complex **4e**).

2.4.   X-ray structure determinations

For the X-ray structure determination; X-ray-quality single crystal of Pt(II) complex [PtCl{$\underline{N}$H=C(Me)N=C(C$_6$H$_4$)$\underline{N}$C=NC(Me)=$\underline{N}$H}] **3a** was obtained by slow evaporation from chloroform. The crystals of **3a** were immersed in cryo-oil, mounted in a MiTeGen loop and measured at 120 K. The X-ray diffraction data were collected on a Bruker KappaApex II or an Agilent Technologies

8

Supernova using Mo Kα radiation (λ = 0.70173 Å). The CrysAlisPro [17] program packages were used for cell refinements and data reductions. The structure was solved by charge flipping method using the SUPERFLIP [18] program. A multi-scan absorption correction based on equivalent reflections (CrysAlisPro) was applied to the data. Structural refinement was carried out using SHELXL2014 [19]. The N-H hydrogen atom (H1) 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 = 0.95-0.98 Å and U_{iso} = 1.2-1.5 U_{eq} (parent atom).

The crystallographic details are summarized in Table 1. Detailed structural parameters are given in supplementary material. CCDC number 1518110 contains 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.

3.   Results and discussion

3.1.   *Reactions of bis(nitrile) Pt(II) complexes 1 with 1,3-diiminoisoindoline 2*

We have recently found [15] that 1,3-diiminoisoindoline, which represents a family of aromatic diimines, exhibits nucleophilic properties toward Pt(II)-bound nitriles (propionitrile and benzonitrile). The stability of the 1,3-diiminoisoindoline and of the products of its addition to nitrile ligands encouraged us to expand this type of reaction to other Pt(II) and Pd(II)-bound nitriles. 1,3-Diiminoisoindoline bears two nucleophilic sp^2-nitrogen centres and one endocyclic amine group, which upon deprotonation might coordinate to Pt(II) or Pd(II) metal centre forming stable *chelated* fused metallacycles (Figure 1).
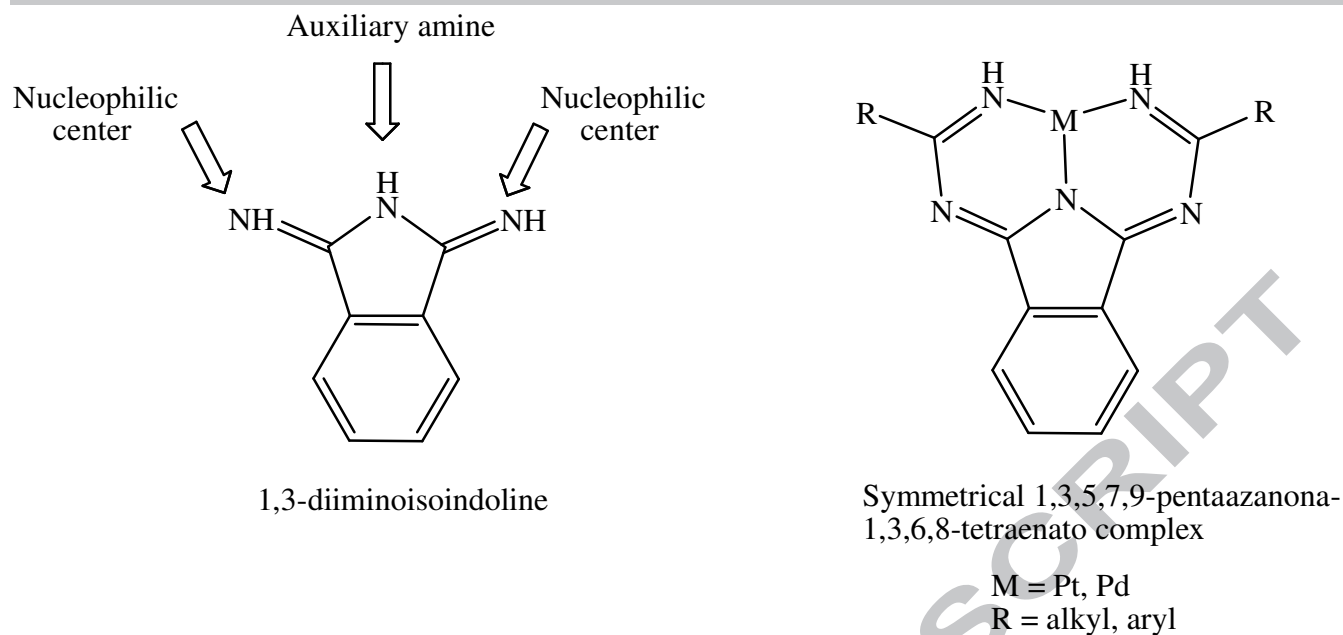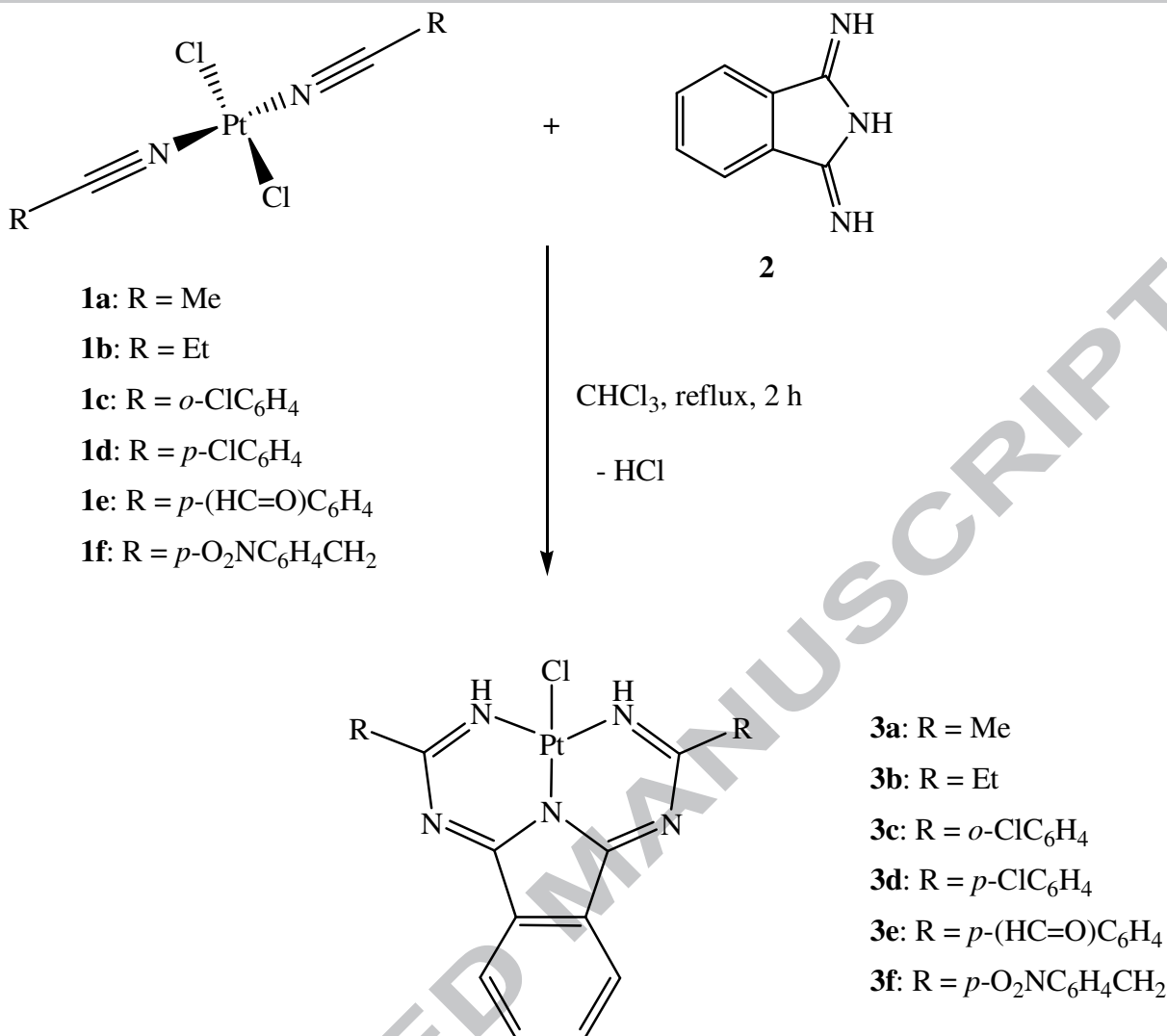
9

Auxiliary amine

Nucleophilic center

Nucleophilic center

1,3-diiminoisoindoline

Symmetrical 1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato complex

M = Pt, Pd
R = alkyl, aryl

Figure 1

Herein, we describe the selective synthesis of new symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes by using various aliphatic and aromatic nitriles as starting bis(nitrile) Pt(II) complexes and 1,3-diiminoisoindoline as the reacting sp^2-nitrogen nucleophile.

The starting Pt(II)-bound nitrile complexes *trans*-[PtCl$_2$(NCR)$_2$] **1** (R = Me (**1a**), Et (**1b**), *o*-ClC$_6$H$_4$ (**1c**), *p*-ClC$_6$H$_4$ (**1d**), *p*-(HC=O)C$_6$H$_4$ (**1e**), *p*-O$_2$NC$_6$H$_4$CH$_2$ (**1f**)) were prepared, in excellent yields (*ca.* 90%), by reaction of PtCl$_2$ with the respective nitrile under heating. Treatment of complexes **1a-f** with one equivalent of 1,3-diiminoisoindoline HN=$\underline{C}$C$_6$H$_4$C($\underline{N}$H)=NH **2**, in refluxing chloroform for 2 h, gives access to the corresponding symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes [PtCl{$\underline{N}$H=C(R)N=C(C$_6$H$_4$)$\underline{N}$C=NC(R)=$\underline{N}$H}] **3a-f** in good yields (65–70 %) (Scheme 1).

10

1a: R = Me
1b: R = Et
1c: R = *o*-ClC$_6$H$_4$
1d: R = *p*-ClC$_6$H$_4$
1e: R = *p*-(HC=O)C$_6$H$_4$
1f: R = *p*-O$_2$NC$_6$H$_4$CH$_2$

CHCl$_3$, reflux, 2 h

- HCl

3a: R = Me
3b: R = Et
3c: R = *o*-ClC$_6$H$_4$
3d: R = *p*-ClC$_6$H$_4$
3e: R = *p*-(HC=O)C$_6$H$_4$
**3f**: R = *p*-O$_2$NC$_6$H$_4$CH$_2$

Scheme 1

In a blank experiment, a prolonged reflux (24 h) of a mixture of one equivalent of acetonitrile and two equivalents of 1,3-diiminoisoindoline in chloroform showed no addition to *cyanocarbon* of acetonitrile and only the starting materials were recovered, indicating the Pt(II)-assisted character of the coupling.

The obtained Pt(II) complexes **3a-f** were characterized by IR, ^{1}H, ^{13}C and DEPT-135 NMR spectroscopies, elemental analyses and also by X-ray diffraction (in the case of **3a**). The IR spectra of complexes **3a-f** do not exhibit the typical $\upsilon(N \equiv C)$ values (2350-2300 cm^{-1} range), while new bands due to $\upsilon(NH)$ and $\upsilon(N=C)$ are observed at *ca.* 3255 and *ca.* 1648 cm^{-1}, respectively. For example, in the ^{1}H NMR spectrum of the complex [PtCl{NH=C(Me)N=C(C$_6$H$_4$)NC=NC(Me)=NH}] **3a**, the signal of the

11

two methyl groups appears as a singlet at δ 2.55, and the NH protons are exhibited at δ 9.80. The ^{13}C NMR spectrum of **3a** shows the characteristic signals of the imine N=C groups at δ 153.1 and 159.8, and the absence of the nitrile N≡C resonance at *ca.* 116 ppm confirms that the nucleophilic addition of 1,3-diiminoisoindoline **2** occurs to both acetonitrile ligands in **1a** (see Experimental Section for more details).

3.2. X-ray structure crystallography

Complex **3a** has a relatively simple molecular structure. The crystal data and structure refinement are given in Table 1, representative diagram is given in Figure 2 and selected bond distances and angles are provided in Table 2. Other relevant features of the structure of **3a** are given as Supplementary Material. The geometry around the Pt ion in **3a** is of square planar type, comprising two fused six-membered metallacycles. Atoms Cl1, Pt1, and N3 are placed on a two-fold rotation axis. Practically planar molecules are forming stacks with metal-π and π-π interactions along the crystallographic c-axis (Figure 3). The shortest atom-atom distances between the adjacent planes are Pt1-C5$^{\#1}$: 3.3575(3) Å, C1-C4$^{\#2}$: 3.3890(4) Å and C3-C3$^{\#1}$: 3.3639(4) Å (#1: -x, 1-y, -z, #2: x,1-y,-1/2+z). The stacks are further supported by weak H-bonds between the NH group and Cl as well as CH$_3$ group and Cl (Figure 3). In the previously published structure **3b**, the metal compounds are also stacked with shortest C-C distances ranging from 3.344 Å to 3.369 Å. In this structure the stacks are supported both by weak CH$_2$-Cl H-bonds and much stronger H-bonds involving water of crystallization [15].

12
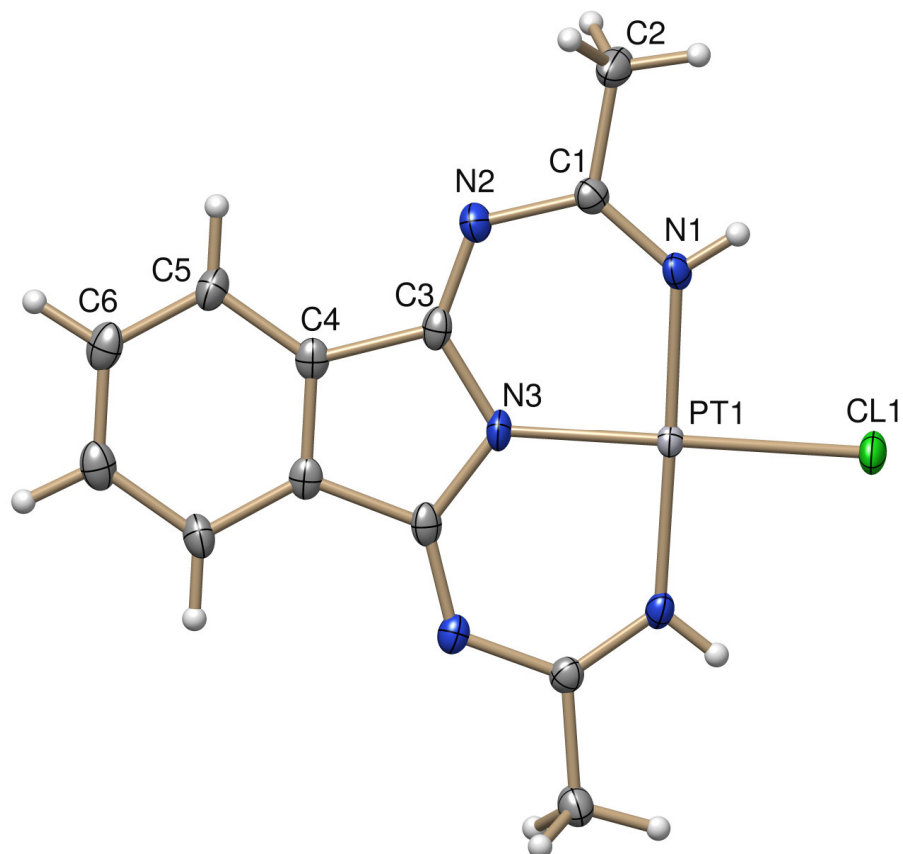
Figure 2. Crystal structure of complex **3a**.
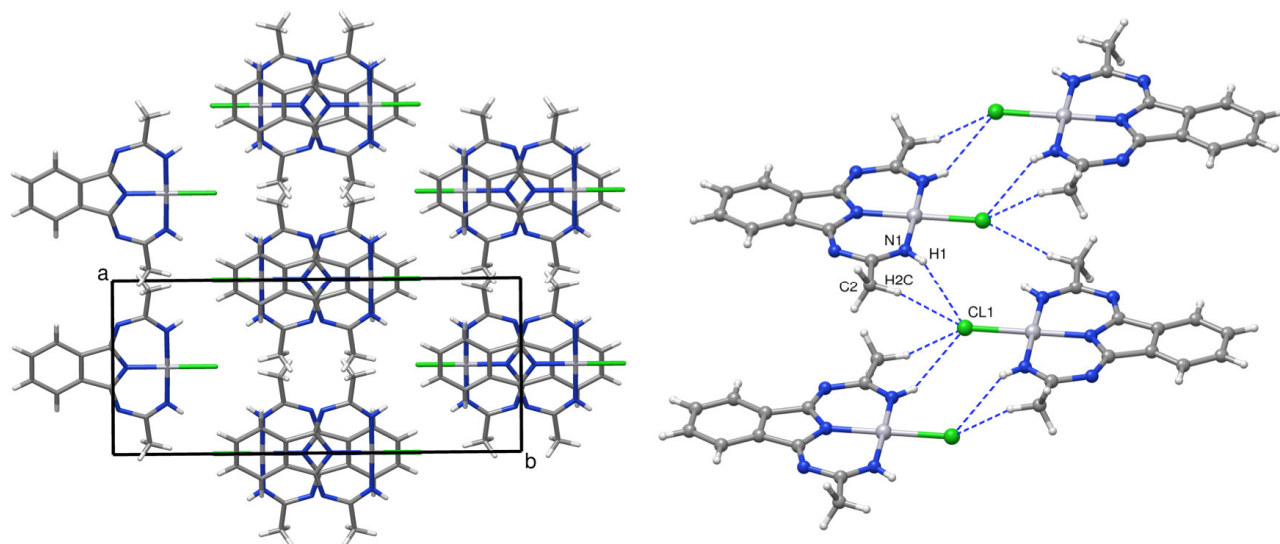
Figure 3. Left: Packing of **3a** along the crystallographic c-axis. Right: H-Bonds in **3a**. N1-H1: 0.83(9) Å, H1···Cl1[#3]: 2.69(9) Å, N1···Cl1[#3]: 3.403(5), N1-H1··· Cl1[#3]: 145(7)°, C2-H2: 0.98 Å, H1··· Cl1[#3]: 2.87, C2···Cl1[#3]: 3.643 Å, C2-H2··· Cl1[#3]: 137° (#3: -x+1/2, -y+1/2, -z+1).

Table 1. Crystal data and structure refinement for complex **3a**.

	3a
empirical formula	$C_{12}H_{12}ClN_5Pt$
Fw	456.81
temp (K)	120(2)
λ(Å)	1.54184
cryst syst	Monoclinic
space group	C2/c
a (Å)	11.8678(5)
b (Å)	19.6347(2)
c (Å)	7.7596(3)
β(°)	135.018(7)
V (Å^3)	1278.13(14)
Z	4
ρ_{calc} (Mg/m^3)	2.374
μ(Kα) (mm^{-1})	22.405
No. reflns.	13958
Unique reflns.	1356
GOOF (F^2)	1.139
R_{int}	0.0747
R1^a ($I \geq 2\sigma$)	0.0313
wR2^b ($I \geq 2\sigma$)	0.0823

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

Table 2. Selected bond lengths [Å] and angles [°] for complex **3a**.

_____

Pt1-N(3)	1.961(6)
Pt1-N(1)#1	1.972(5)
Pt1-N(1)	1.972(5)
Pt1-Cl1	2.3178(16)
N(3)-Pt1-N(1)	89.34(11)
N(1)#1-Pt1-N(1)	178.7(2)
N(3)-Pt1-Cl1	180.0
N(1)-Pt1-Cl1	90.66(11)

_____

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

14

3.3.   Reactions of bis(nitrile) Pd(II) complexes 4 with 1,3-diiminoisoindoline 2

Here, we report the selective synthesis of new symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pd(II) complex by using *trans*-[PdCl$_2$(NCMe)$_2$] as the starting bis(nitrile) Pd(II) complex and 1,3-diiminoisoindoline as the reacting *sp^2*-nitrogen nucleophile.

The starting Pd(II)-bound acetonitrile complex *trans*-[PdCl$_2$(NCMe)$_2$] **4a** was prepared, in excellent yield (89%), by reaction of PdCl$_2$ with acetonitrile under heating. Treatment of complex **4a** with one equivalent of 1,3-diiminoisoindoline **2**, in refluxing acetonitrile for 2 h, gives access to the symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pd(II) complex [PdCl{NH=C(Me)N=C(C$_6$H$_4$)NC=NC(Me)=NH}] **5a** in good yield (65 %) (Scheme 2, reaction *a*).

The IR spectrum of complex **5a** do not exhibit the typical υ(N≡C) values (2350-2300 cm^{-1} range), while new bands due to υ(NH) and υ(N=C) are detected at 3440 and 1639 cm^{-1}, respectively. In the ^{1}H NMR spectrum of **5a**, the signal of the two methyl groups appears as a singlet at δ 2.57, and the N*H* protons are exhibited at δ 10.20 and 10.33. The ^{13}C NMR spectrum shows the characteristic signals of the imine N=*C* groups at δ 156.3 and 164.8, and the absence of the nitrile N≡*C* resonance at *ca.* 116 ppm confirms that the nucleophilic addition of 1,3-diiminoisoindoline **2** occurs to both acetonitrile ligands in **4a**.

We have also studied the reaction of 1,3-diiminoisoindoline with other bis(nitrile) complexes *trans*-[PdCl$_2$(NCR)$_2$]. Hence, the careful NMR analysis of the products of the reaction of *trans*-[PdCl$_2$(NCR)$_2$] **4** (R = Ph (**4b**), *p*-MeC$_6$H$_4$CH$_2$ (**4c**), *p*-(HC=O)C$_6$H$_4$ (**4d**), *p*-O$_2$NC$_6$H$_4$CH$_2$ (**4e**)) with **2** shows the formation of a number of unidentified products (in the case of **4b** and **4d**), or the free nitriles *p*-tolylacetonitrile and *p*-nitrophenylacetonitrile (resulting from the decomposition of the complexes **4c** and **4e**, respectively) together with a number of uncharacterized products (Scheme 2, reaction *b*). The ^{13}C NMR spectra show the absence of the characteristic signals of the imine N=*C* groups at δ 153 and 165.
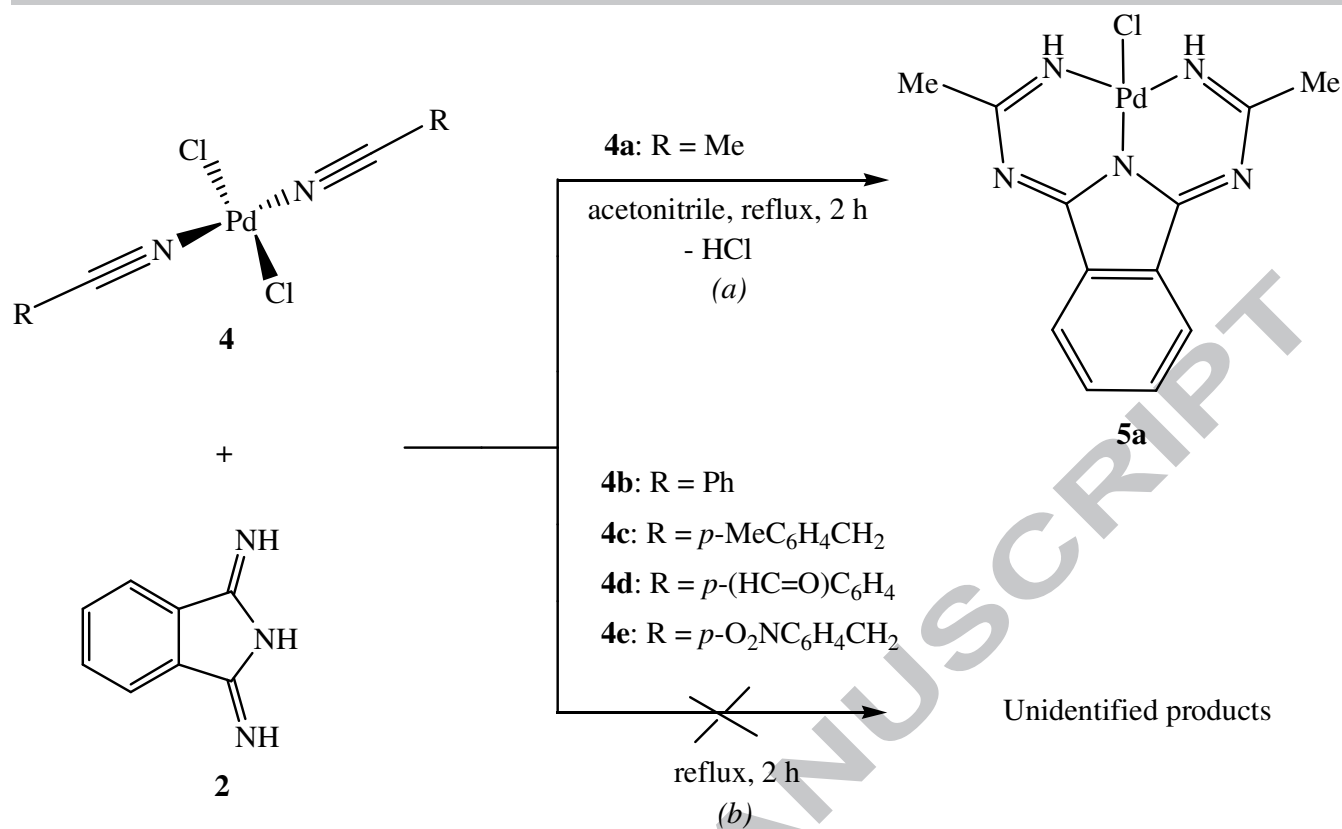
Scheme 2

3.4. *UV-vis absorption spectra*

The absorption spectra of the Pt(II) complexes **3a** and **3b** exhibit a band at 400-430 nm typical of a metal-to-ligand charge transfer (MLCT) low energy transition, and intrinsic of the d^8 platinum complexes. The bands located around 330 nm are more ligand-centered and, due to the solvent cut-off, it was not possible to observe the highest energy absorption bands, which should be located below 250 nm for this type of complexes [14], and correspond to $^1(\pi-\pi^*)$ IL (intraligand) transitions.

The absorption data (maximum absorption wavelengths and corresponding molar absorption coefficients) are summarized in Table 3.

Table 3. Wavelengths of the absorption maxima, respective molar absorption coefficients, luminescence quantum yields and lifetimes for Pt(II) complexes **3a** and **3b**.

	λ_{max}/nm (ε/M^{-1} cm^{-1}), CH$_2$Cl$_2$	λ_{em}/nm, CH$_2$Cl$_2$	Φ_L / x10^{-3}, CH$_2$Cl$_2$	τ / ns

16

|				
3a	334 (8930) 404 (4225) 428 (3995)	607	3.1	70[a]
3b	318 (8215) 330 (8587) 401 (4355) 426 (4375)	605	3.6	82[a] (95)[b]

[a] in chloroform; [b] in dichloromethane.

3.5.   *Luminescence emission spectra*

Both compounds are emissive in dichloromethane solution, and exhibit very similar emission spectra, luminescence quantum yields and lifetimes. This might be due to the structural similarity between the two compounds, which only differ by one carbon atom in two of the imine substituents. The emission data are collected in Table 3. Absorption, emission and excitation spectra of both complexes are represented in Figures 4 and 5.
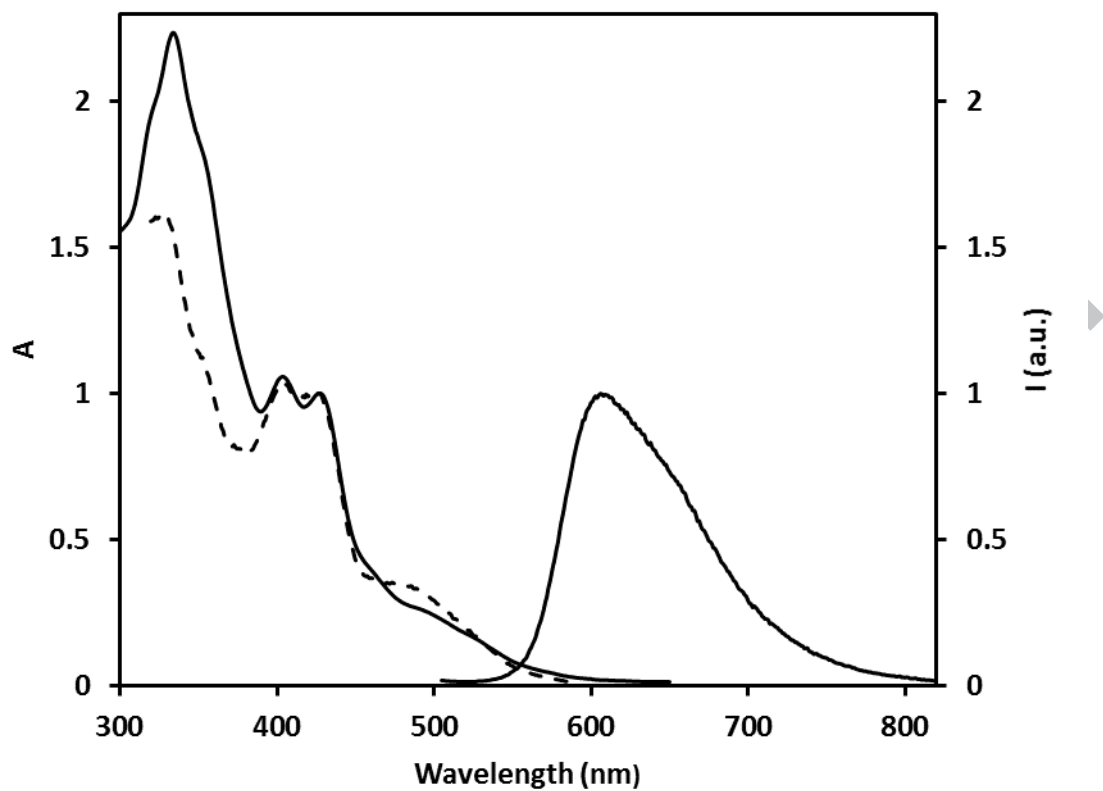
Figure 4. Normalized absorption, emission (solid lines) and excitation (dashed line) spectra of compound **3a** in CH_2Cl_2. λ_{exc} = 428 nm.
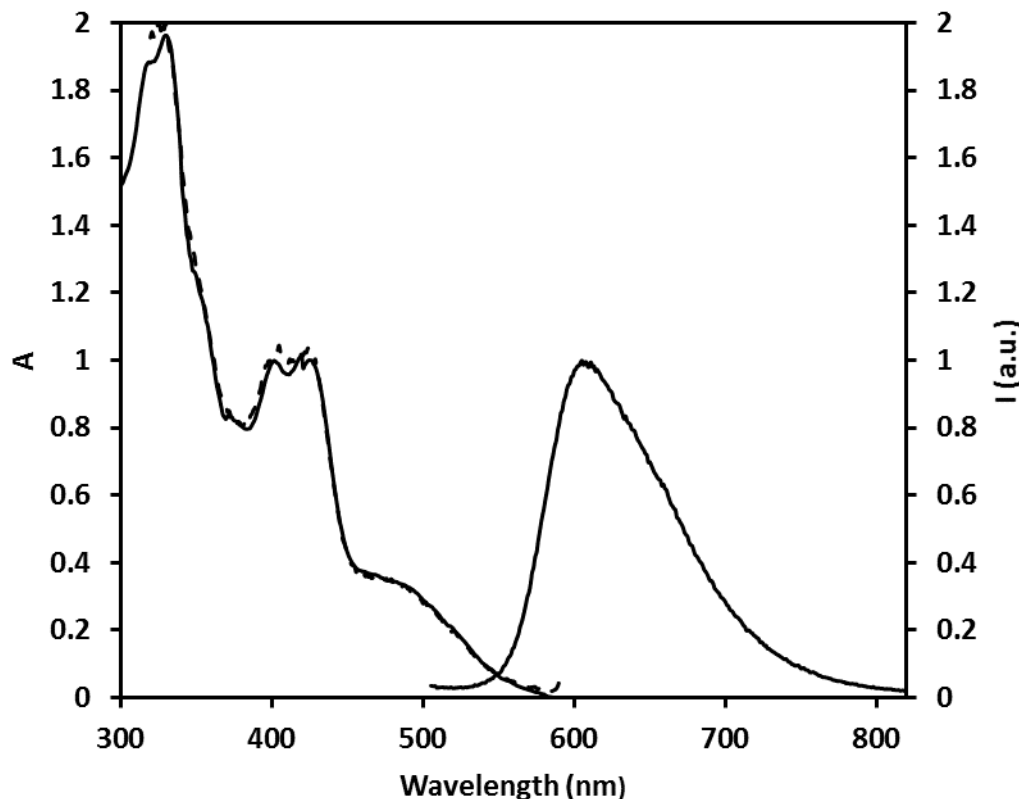
Figure 5. Normalized absorption, emission (solid lines) and excitation (dashed line) spectra of compound **3b** in CH_2Cl_2. $\lambda_{exc} = 426$ nm.

By comparison of the luminescence lifetimes assessed for these compounds with those collected for Pt(II) imidoylamidinates [14], it is possible to observe that the former are several orders of magnitude lower. This might be due to the fact that Pt(II) complexes **3a** and **3b** exhibit a smaller degree of electronic delocalization, which ultimately governs the lifetime of the emissive triplet state. It is worth mentioning that degassing produced no effect on their lifetimes and quantum yields.

3.6.   Solid state luminescence

Compounds **3a** and **3b** also exhibited luminescence in solid state. The characterization was performed following the procedure described in section 2.1, and the resulting emission spectra are depicted in Figure 6.
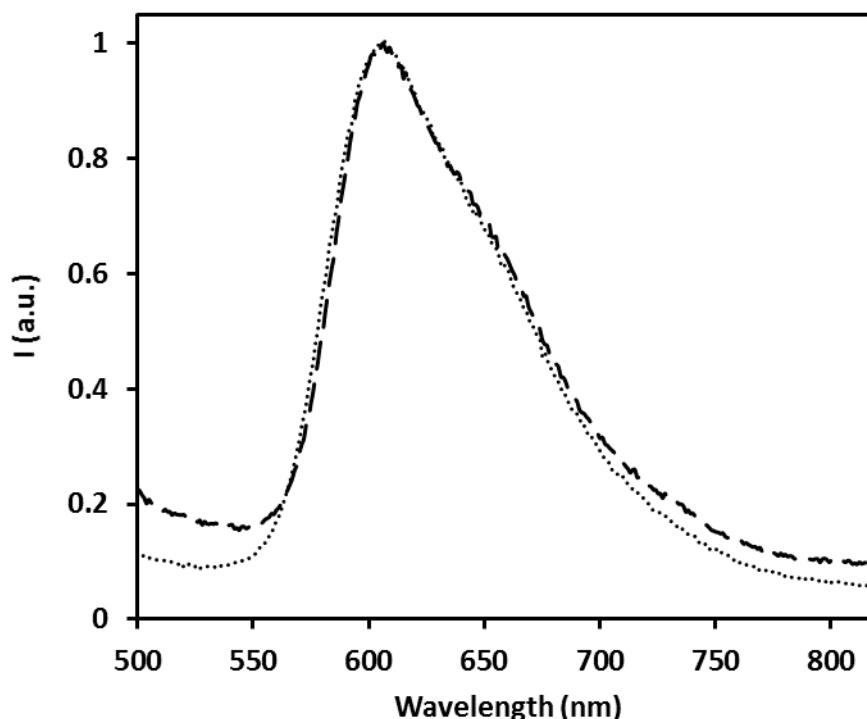
Figure 6. Normalized emission (dashed line) spectra of compounds **3a** (dashed line) and **3b** (dotted line) in polystyrene film. λ_{exc} = 441 nm.

The spectra are very similar to the ones obtained in solution for both compounds, except for the slight elevation of the baseline, which is common for solid samples, owing to scattering. Regarding luminescence lifetimes, a significant increase occurs in the solid state, a common lifetime of 160 ns being measured for both **3a** and **3b**. Immobilization of the compounds in the solid matrix significantly reduces collisional quenching, hence increasing the excited state lifetime.

4. Conclusions

The results of this work can be summarized under four perspectives. First, the reaction between *trans*-[PtCl$_2$(NCR)$_2$] **1** and 1,3-diiminoisoindoline **2** affords (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes **3**. Second, we achieved the selective synthesis of new symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pd(II) complex **5a** by using *trans*-[PdCl$_2$(NCMe)$_2$] **4a** and 1,3-diiminoisoindoline **2**, and the system represents a novel reactivity mode which has never been reported so far. Third, the developed synthetic methods operate under mild conditions (reflux, 2 h), furnish pure symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) and Pd(II) complexes, and, in contrast to the preparation of (1,3,5-triazapentadienato)Ni(II) complexes [7a], does not need the use of a base. Fourth, the emissive Pt(II) complexes **3a** and **3b** exhibited significantly lower luminescent

20

lifetimes in solution when compared to their Pt(II) imidoylamidinate analogues [14], which is a consequence of a smaller electronic delocalization in the former. Furthermore, absorption spectra allowed the assignment of the typical [3]MLCT transition bands, characteristic of this type of transition-metal complexes.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article (X-ray crystallographic data and copies of ^{1}H, ^{13}C and DEPT-135 NMR spectra) can be found, in the online version, at http://dx.doi.org/.....

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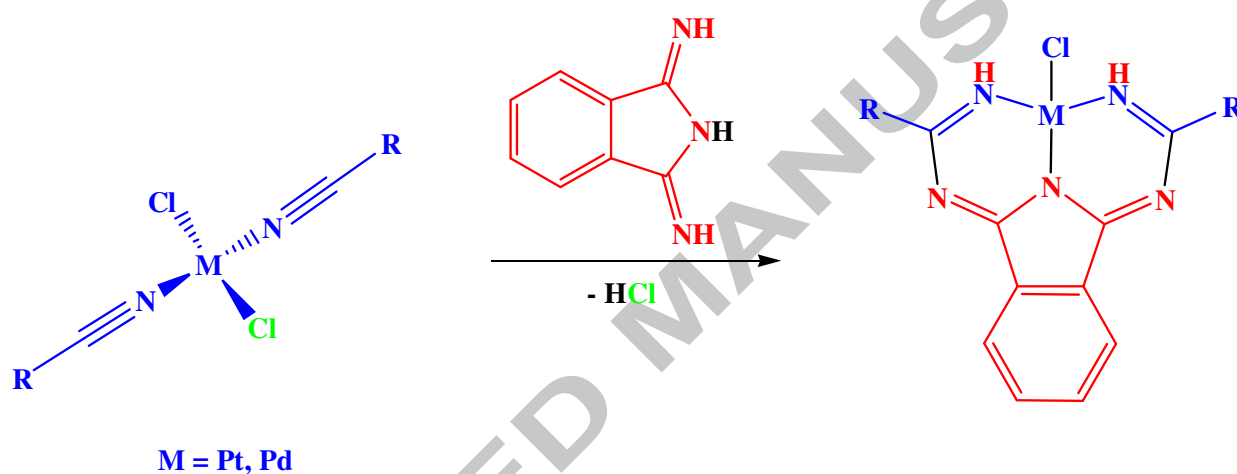
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Pt(II) and Pd(II)-assisted coupling of nitriles and 1,3-diiminoisoindoline: Synthesis and luminescence properties of (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) and Pd(II) complexes

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Graphical abstract

Synopsis

Novel (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) and Pd(II) complexes were prepared by nucleophilic additions of 1,3-diiminoisoindoline to Pt(II) or Pd(II)-bound nitriles, respectively. Photophysical characterization allowed elucidation of the electronic structure of some of the complexes.