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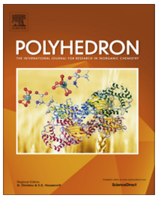

Pt(II) and Pd(II)-assisted coupling of nitriles and 1,3-diiminoisoindoline: Synthesis and luminescence properties of (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) and Pd(II) complexes

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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=CC$_6$H$_4$C(*N*H)=NH **2** gives access to the corresponding (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes [PtCl{*N*H=C(R)N=C(C$_6$H$_4$)*N*C=NC(R)=*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{*N*H=C(Me)N=C(C$_6$H$_4$)*N*C=NC(Me)=*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{*N*H=C(Me)N=C(C$_6$H$_4$)*N*C=NC(Me)=*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.

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–Vis 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=CC$_6$H$_4$C

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(*NH*)=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

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 35,000, 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

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).

2.2.2.1. 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*$H_{aromatic}$).

*2.2.2.2. 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*≡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 (*C*$H_{aromatic}$).

2.2.2.3. p-Cyanobenzaldehyde N≡C(p-(HC=O)C$_6$H$_4$). ^{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, *H*C=O). ^{13}C NMR (CDCl$_3$), δ: 117.6 and 117.7 (*C*≡N), 129.9, 132.9, 138.7 ($C_{aromatic}$), 190.6 (H*C*=O). DEPT-135 NMR (CDCl$_3$), δ: 129.9, 132.9 (*C*$H_{aromatic}$), 190.6 (H*C*=O).

*2.2.2.4. 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, *H*C=O). ^{13}C NMR (CDCl$_3$), δ: 113.9 and 115.8 (*C*≡N), 129.9, 134.6, 140.3 ($C_{aromatic}$), 190.0 (H*C*=O). DEPT-135 NMR (CDCl$_3$), δ: 129.9, 134.6 (*C*$H_{aromatic}$), 190.0 (H*C*=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.

*2.2.3.1. [PtCl{NH=C(Me)N=C(C$_6$H$_4$)NC=NC(Me)=NH}] (**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, N*H*). ^{13}C NMR