COMMUNICATION

New N^C^N-coordinated Pd(II) and Pt(II) complexes of a tridentate N-heterocyclic carbene ligand featuring a 6-membered central ring: synthesis, structures and luminescence

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**We describe Pd(II) and Pt(II) complexes of an N^C^N-coordinating pincer-like ligand featuring two lateral pyridine rings and a 6-membered carbene core. Their crystal structures display 1-dimensional chains with short π-π and M(II)···M(II) interactions. Such interactions also impact on the photophysical properties, with the Pt(II) complex being luminescent in the solid state at room temperature.**

Metal complexes of pincer ligands are of crucial importance in modern organometallic chemistry.[1] The term 'pincer' refers to monoanionic tridentate ligand platforms that feature a central connection between the monoanionic site and the metal, and encompasses many *ECE* cyclometallated complexes (e.g. *E* = P, N, S). In particular, cyclometallated palladium(II) and platinum(II) pincer complexes have received a great deal of attention due, in particular, to their unique catalytic and photophysical properties respectively.[2,3] For instance, cyclometallated platinum(II) pincer complexes are of interest in many photonic applications such as OLEDs,[4] sensors,[5] and photocatalysts.[6] Platinum(II) complexes with N^C^N-coordinating tridentate ligands have proven to be attractive phosphors in OLED devices, for example, those based on 1,3-dipyridylbenzene (dpybH) and related compounds.[7] We note also an emerging family of C^C and C^C^C platinum(II) complexes with promising luminescent properties.[8] Related palladium(II) pincer complexes have been found to be excellent pre-catalysts in various organic transformations.[9]

On the other hand there is currently a growing interest in the design of transition metal complexes of N-heterocyclic carbene (NHC) ligands, owing to the superior stability of such complexes and the possibility of obtaining interesting materials with attractive catalytic or luminescence properties. Tridentate *ECE* ligands featuring a central carbene donor resemble *ECE* pincer ligands, but they are charge-neutral as opposed to anionic. Only a few, relatively unstable, palladium complexes with an NCN pincer carbene have been reported, consisting of a central imidazolylidene ring with two N-containing wingtip donor fragments, such as pyridine or diisopropylamine.[10] We note that there is no report of either Pd(II) or Pt(II) complexes with N^C^N-coordinating ligands

incorporating a six-membered NHC central core. We envisage that the use of such NHC-based ligands might give rise to complexes with electronic features that differ from those with conventional, anionic N^C^N-coordinating ligands such as dpyb⁻. Such differences might impact on the luminescent or catalytic properties, for instance, whilst the resulting complexes are cationic rather than neutral.

In this communication, we wish to report the synthesis and characterization of two unprecedented complexes of Pd(II) and Pt(II) with a rare bis-chelating tridentate N^C^N ligand **L**, in which *the central C nucleophile is a six-membered NHC core* (Scheme 1). We believe that the target complexes may find various applications. Compound **L** is obtained from its proligand N,N'-bis(2-pyridyl)-tetrahydropyrimidinium hexafluorophosphate **LH⁺PF₆⁻** (**1**). As far as we are aware, only two complexes of ligand **L** have been reported previously, both with Ru(II).[11] We were intrigued to explore the coordination behaviour of this potentially tridentate ligand with the d⁸ Pd(II) and Pt(II) ions, and how such complexes would compare with those of the structurally closely related, but anionic, N^C^N-coordinating ligand dpyb⁻, e.g. Pt(dpyb)Cl (Scheme 1).
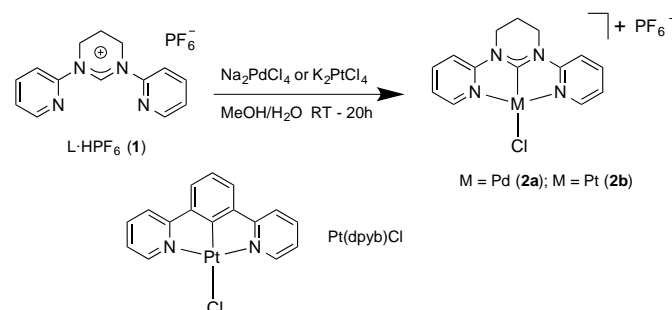
Scheme 1. Synthesis of complexes [Pd**L**Cl]PF₆ (**2a**) and [Pt**L**Cl]PF₆ (**2b**) from the proligand **LH⁺PF₆⁻** (**1**). The structure of [Pt(dpyb)Cl] is also shown for comparison.

During our initial attempts to obtain the desired complexes, we discovered that treatment of the proligand **L·HPF₆** (**1**) with metallic salts under alkaline conditions in protic solvents led to unidentified decomposition products. The target compounds

[Pd**L**Cl]PF$_6$ (**2a**) and [Pt**L**Cl]PF$_6$ (**2b**) were finally obtained by refluxing **1** with Na$_2$PdCl$_4$ or K$_2$PtCl$_4$, respectively, in a mixture of methanol and water (see SI for experimental procedures). Cyclometallation thus occurs through direct C–H bond activation of the pyrimidinium moiety. Though unoptimised, the yields are rather low, partly due to the very poor solubility of these novel materials, and probably also to the formation of significant quantities of unidentified dark brown insoluble material during the reactions, presumed to be platinum metal. The identity of the complexes was established by spectroscopic methods and by elemental analyses. Moreover the structures of these compounds were unequivocally ascertained by single crystal X-ray diffraction analyses. The ^{1}H NMR spectrum of **2a** in CD$_3$CN exhibits a set of four signals in the aromatic region at δ = 7.38–8.58 ppm. We note the presence of two signals at δ = 3.87 ppm and δ = 2.45 ppm in the aliphatic region due to the protons of the central ring. The spectrum also confirms the absence of the tetrahydropyrimidinium proton H$_a$ (Figure S1) confirming metallation of the central ring of the proligand. ^{19}F-NMR and infrared spectroscopy confirm the presence of the PF$_6$ anion. The platinum(II) counterpart (**2b**) shows similar NMR features but, in addition, ^{195}Pt satellites are now visible for the signal of the α-protons of the pyridyl rings. In order to confirm the molecular identity of these new compounds, suitable crystals for an X-ray diffraction analysis were grown by slow evaporation of acetonitrile solutions of the complexes. Both compounds **2a** and **2b** crystallize in the orthorhombic P*nma* space group with three molecules in the unit cell and one acetonitrile solvent molecule.[12] The structures are in agreement with the proposed formulae. They exhibit a Pd(II) (**2a**) or Pt(II) (**2b**) centre in a slightly distorted square planar environment. In both cases the metal centre is bis-chelated by one tridentate ligand **L** and coordinated to a chloride anion to complete the coordination sphere. The Pd–N and Pt–N bonds lie within the normal range of reported values in related complexes. Striking features of these structures are the very short Pd–C (1.890 Å) and Pt–C (1.889 Å) bonds, resulting in a strong *trans*-influence of the NHC core that is also manifest in the very long Pd–Cl (2.370 Å) and Pt–Cl (2.371 Å) bonds. These important features may play a prominent role in the luminescent and/or catalytic properties of these species.

The [Pd**L**Cl]$^+$ cations of **2a** self-organize in the crystal in a head-to-tail fashion to form 1D supramolecular chains (Fig. 1). Analysis of the intermolecular distances reveals the presence of π–π interactions between the pyridyl rings (d$_{plane / centroid}$ = 3.320 Å) and Pd(II)···Pd(II) distances (3.363 Å) at the limit of the van der Waals contact for palladium ions (3.26 Å). We note that Pd(II)···Pd(II) metallophilic interactions are very rare in comparison to the Pt(II)···Pt(II) analogues. Similarly, the cations of **2b** self-organize in the crystal in a head-to-tail fashion to describe 1D supramolecular chains. Analysis of the intermolecular packing of **2b** reveals the presence of π–π interactions between the pyridyl rings (d$_{plane / centroid}$ = 3.323 Å) and Pt(II)···Pt(II) interactions (3.362 Å). Such interannular and intermetallic interactions are well known to impact the luminescent properties of many platinum(II) compounds.[13,14] In particular, Pt(dpyb)Cl and its derivatives are known to form highly luminescent aggregates and/or excimers involving face-to-face intermolecular interactions,[15] and we anticipated that such interactions might impact strongly upon the properties of the new complexes **2a** and **2b**.
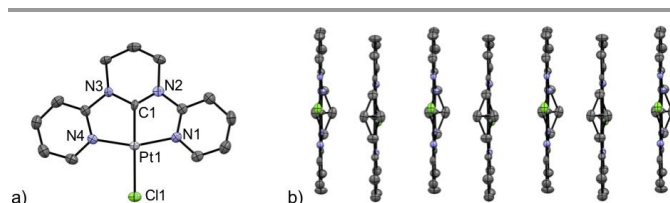

Figure 1. View of the cation in [Pt**L**Cl]PF$_6$·CH$_3$CN (**2b·CH$_3$CN**) (a) and intermolecular packing of the cations along a 1D chain arising from Pt(II)···Pt(II) and π–π interactions (b). Pd1-Cl1=2.370; Pt1-Cl1=2.371; Pd1-C1=1.890; Pt1-C1=1.889; Pd1-N1=2.026; Pt1-N1=2.016; Pd1-N4=2.260; Pt1-N4=2.023.

The UV-visible absorption spectra of the proligand **1** and its Pd(II) and Pt(II) complexes were recorded in acetonitrile solution (Figure S6 and Table 1). The spectrum of **1** shows intense bands in the region 250–280 nm (ε > 14000 M^{-1}cm^{-1}), attributed to π–π□ transitions, together with an even more intense band at 303 nm. Like **1**, the two complexes also display strong bands around 250–260 nm, roughly twice as intense as those of **1**, but, unlike **1**, they do not feature any band around 300 nm. Thus, we tentatively assign the band at 303 nm in **1** to an excited state that spans the :N–C=N–py conjugated unit, this conjugation being broken in the complexes, where π–π* absorptions are thus limited to the pyridyl rings (in the 250–260 nm region).

On the other hand, the two complexes display additional bands at longer wavelengths, > 330 nm, that have no counterpart in the proligand **1**. They have extinction coefficients in the 10^3–10^4 range, clearly much too high to be attributable to metal-centred, d–d transitions. Based on the well-known behaviour of complexes of related tridentate ligands such as terpyridine (tpy)[16] and 1,3-dipyridylbenzene (dpybH),[15,17] these bands are likely to be due to charge-transfer transitions of MLCT and LLCT nature, with the pyridyl rings acting as acceptors. The bands extend out to longer wavelength for the Pt(II) complex **2b** compared to the Pd(II) analogue **2a**, which would be consistent with the greater ease of oxidation of Pt(II) compared to Pd(II). However, we cannot rule out that the weaker bands at 404 and 383 nm for the Pt(II) complex (ε = 800) are due to the direct S$_1$ → T$_1$ transition, facilitated by the large spin-orbit coupling (SOC) of the Pt centre, by analogy with the behaviour of Pt(dpyb)Cl. Such bands are typically not expected to be observable for the Pd(II) analogues, owing to the much smaller SOC constant of palladium compared to platinum. The low-energy bands result in the Pt(II) complex **2b** being yellow in colour, whereas the Pd(II) analogue **2a** is colourless.

Table 1   UV-visible absorption data for proligand **L·HPF$_6$** (**1**) and its Pd(II) and Pt(II) complexes, **2a** and **2b** respectively, in MeCN at 298 K.

	λ$_{max}$ / nm (ε / M^{-1}cm^{-1})
1	256 (20100), 266 (17000) 277 (14700), 303 (27400)
2a	249 (47500), 269sh (13900), 291 (9800), 344sh (6400), 360 (7700), 376 (5800)
2b	255 (42700), 327sh (9000), 337sh (12100), 383 (1200), 401 (800)

No significant luminescence can be detected from deoxygenated acetonitrile solutions of the metal complexes **2a** or **2b** at room temperature. However, in the solid state at room temperature, the platinum compound **2b** exhibits an intense

orange luminescence under long-wave UV irradiation, whereas the Pd(II) complex does not. The emission of **2b** is easily visible to the naked eye (Figure S7), whilst the recorded spectrum shows a broad, structureless band centred at 570 nm (Figure 2). The temporal decay of the luminescence follows mono-exponential kinetics, with a lifetime of 480 ns. This long value is indicative of a triplet nature to the emissive excited state, the formally spin-forbidden $T_1 \rightarrow S_0$ process being promoted by the high spin-orbit coupling associated with the Pt(II) centre.
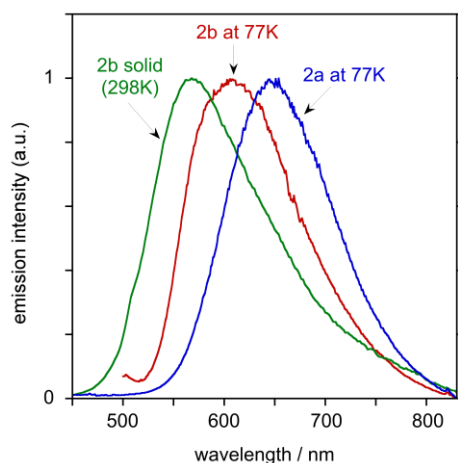
Figure 2. Luminescence spectra of **2b** in the solid state at 298 K (green line) and of **2b** and **2a** in butyronitrile glass at 77 K (red and blue lines respectively).
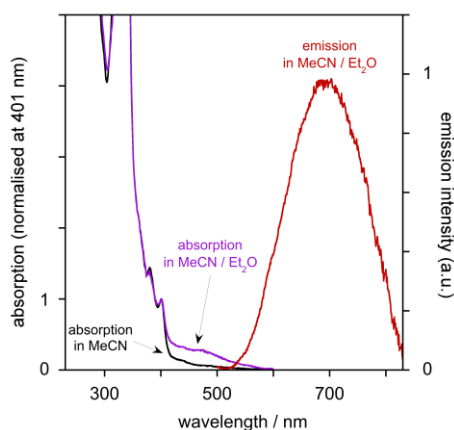
Figure 3. Luminescence spectrum recorded for a solution of **2b** in MeCN / Et₂O (1:1) at 298 K (red line), together with the corresponding absorption spectrum (purple line). The absorption spectrum in MeCN alone is also shown for comparison (black line).

Interestingly, we found that, although acetonitrile solutions of **2b** are not luminescent at ambient temperature, the addition of diethyl ether to such a solution (10^{-4} M) leads to red emission being detectable (Figure 3). Over a period of some hours, precipitation is observable, but in the initial phase after addition of ether, the solution remains free of particulates (as evident from the transmission monitored by UV-visible spectroscopy at $\lambda > 600$ nm). Evidently, the addition of the less

polar solvent induces the aggregation of the complex, with the aggregates presumably small enough to remain soluble initially, before precipitation occurs. The UV-visible spectrum of the mixed acetonitrile / ether solution of **2b** is similar to that in acetonitrile alone, but there is evidence of an additional broad, weak absorption at low-energy ($\lambda_{max} \sim 465$ nm, Figure 5), behaviour quite typical of many other platinum(II) complexes that are known to aggregate through Pt⋯Pt interactions.[14] In these instances, such interactions destabilise the HOMO, whilst interligand interactions may concomitantly stabilise the LUMO, both of which effects lead to a red-shifted absorption.

The emission maximum and luminescence lifetime recorded for the MeCN / Et₂O solution are 690 nm and 1.1 µs respectively, values which are quite different from those recorded in the solid (see above). Presumably the aggregate species formed in solution involve different intermolecular interactions from those in the solid as isolated. We note that subtle differences in the packing of Pt(dpyb)Cl derivatives have previously been shown to lead to very different emission maxima for the same complex. For example, two different, structurally-characterised polymorphs of Pt(Br-dpyb)Cl – differing in the rate at which they crystallised from CHCl₃ – were found to have emission maxima of 498 nm and 670 nm in the solid state (Br-dpyb = 4-bromo-1,3-dipyridylbenzene).[18] A similar effect may be at work in the present instance, leading to the quite different emission maxima according to the arrangement of molecules in the species formed.

Further evidence of the subtlety of the effect of intermolecular interactions emerges from the behaviour of the complexes at 77 K. Owing to the lack of opacity of frozen acetonitrile, we were obliged to use butyronitrile for the purpose of recording low-temperature spectra in glasses. The spectrum of the Pt(II) complex **2b** under these conditions displays a broad emission band with $\lambda_{max} = 610$ nm, $\tau = 4.2$ µs (Figure 2). It would be unlikely for isolated molecules to emit at lower energy than those in the solid, since intermolecular interactions typically destabilise occupied metal-based orbitals and stabilise ligand-based orbitals in Pt(II) complexes, as noted above. Given that there is no change in the 77 K lifetime or spectrum upon dilution, other than a diminution of intensity, we therefore tentatively suggest that the isolated molecules may be non-luminescent even at 77 K, and that the observed emission under these conditions may arise from aggregates similar to those formed in MeCN / Et₂O at room temperature, blue-shifted through rigidochromic effects.

Interestingly, the Pd(II) complex **2a** is also quite intensely luminescent in butyronitrile at 77 K, $\lambda_{max} = 650$ nm (Figure 2). The recorded luminescence lifetime is 140 µs. The much longer value compared to **2b** is typical of the smaller spin-orbit coupling of Pd(II) compared to Pt(II), such that the $T_1 \rightarrow S_0$ transition remains more firmly forbidden.

Conclusions

In summary we have reported the preparation of two novel Pd(II) and Pt(II) complexes with a rare N^C^N tridentate ligand exhibiting a six-membered NHC central core. These compounds show very short Pd–C and Pt–C bond distances that are expected to play a prominent role in the catalytic properties of these species, through the correspondingly very strong *trans*-effect exerted by the carbene centre, for example, as pre-catalysts in organic transformations. Our preliminary photophysical results show that such N-heterocyclic carbene-based tridentate ligands can allow access to Pd(II) and Pt(II)

complexes that are luminescent. Intermolecular interactions are clearly crucial, and further work on a range of derivatives – both modified in the tridentate ligand and incorporating monodentate ligands other than chloride – will be required to unravel the processes involved. Our future efforts will be devoted to investigate in more detail the interplay between structure and photophysical properties of these new compounds.

Notes and references

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† Electronic Supplementary Information (ESI) available: details of experimental procedures and NMR spectra. CIF files containing crystallographic data of complexes **2a** and **2b** are available at CCDC 1479722 and 1479723.

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