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New Members of the 1,3-Di(2-pyridyl)benzene Pro-Ligand Family Bearing Tri- or Tetra-Phenylethylene and Related Platinum(II) Complexes †

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† In memoriam of Bertrand Carboni, a great chemist full of humanity.

Abstract

1,3-di(2-pyridyl)benzene (dpybH) is a fascinating pro-ligand which is structurally similar to terpyridine but the central N atom is replaced by a CH moiety; when CH deprotonation occurs upon binding to a metal atom, then a cyclometallated compound is formed in which the *N^C^N*-bound ligand is isoelectronic with terpyridine, but it is an anionic ligand rather than a neutral ligand. In this study we prepared and thoroughly characterized two new pro-ligands, namely 1,3-bis(4-triphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene and 1,3-bis(4-tetraphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene, which open the doors for new *N^C^N* metal complexes. The related platinum(II) complexes, characterized by a weak emission in solution, were also synthesized.

Keywords: 1,3-bis(2-pyridyl)benzene; tetraphenylethylene; triphenylethylene; platinum(II) complexes

1. Introduction

Polypyridyl ligands have a fundamental role in modern coordination chemistry [1]. In fact, bipyridine has been called "the most widely used ligand" [2], with a ubiquitous number of related coordination compounds, with the terdentate ligand terpyridine following not far behind [3–5]. Metal complexes bearing these ligands are highly stable with respect to metal dissociation, due to the synergistic combination of p-accepting heterocycles and s-donating nitrogen atoms coupled with the presence of five-membered chelating rings; moreover, the same properties favour light absorption—and in some cases emission—in the visible region [1]. Another fascinating pro-ligand is the 1,3-di(2-pyridyl)benzene (dpybH) which is structurally similar to terpyridine but the central N atom is replaced by a CH moiety. When CH deprotonation occurs at this position upon binding to a metal atom, a cyclometallated compound is formed in which the *N^C^N*-bound ligand is isoelectronic with terpyridine; however, it is an anionic ligand rather than a neutral ligand. Sauvage et al. reported the first example of a cyclometallated complex with a dpyb ligand in 1991 [6]. They synthesized the complex $[Ru(ttpy)(dpyb)]^+$ (ttpy = 4′tolyl-2,2′:6′2″-terpyridine), an analogue of the related

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bis-terpyridyl ruthenium(II) complex prepared earlier [7]. Cyclometallation was found to have a profound effect on the redox and excited-state properties of this complex compared to those of the terpyridyl analogue. Following this pioneering report, Sauvage and their co-workers prepared the corresponding cyclometallated osmium(II) complex [8]. Since then, a lot of coordination compounds bearing the dpyb ligand with other metals such as iridium(III), rhodium(III), platinum(II), palladium(II), gold(III) have been prepared [1].

Whereas ruthenium(II), osmium(II) and platinum(II) give a terdentate *N^C^N* binding mode in which cyclometallation occurs at C^2 (Figure 1a), iridium(III), rhodium(III) and palladium(II) tend to give a *N^C* binding mode with C^4 cyclometallation (Figure 1b) although the latter process can be inhibited with a suitable modified dpyb ligand, allowing the *N^C^N* binding mode to be obtained with these metal ions too (Figure 1c). The observation of the dimetallic complex $[Ru(ttpy)(m\text{-}dpyb\text{-}dpyb)Ru(ttpy)]^{2+}$ (Figure 1d) during the formation of $[Ru(ttpy)(dpyb)]^{+}$ [6] led to the preparation of various dimetallic coordination compounds including heterometallic (e.g., Ru-Os) dimers with mixed valency [9].

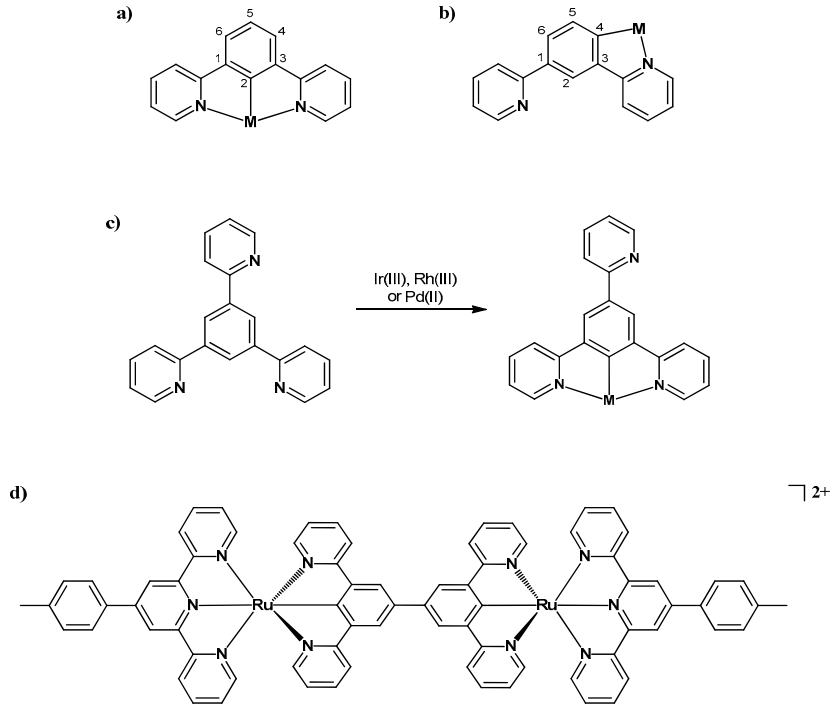


Figure 1. (**a**) *N^C^N* binding mode with cyclometallation at C^2. (**b**) *N^C* binding mode with cyclometallation at C^4. (**c**) The three C-H bonds in the central ring of 1,3,5-tri(2-pyridyl)benzene are equivalent, ensuring *N^C^N* binding mode of Ir(III), Rh(III) and Pd(II) which would otherwise cyclometallate at C^4/C^6. (**d**) Structure of $[Ru(ttpy)(m\text{-}dpyb\text{-}dpyb)Ru(ttpy)]^{2+}$.

The pioneering reports of Sauvage et al. established the great potential of 1,3-di(2-pyridyl)benzene as a cyclometallating *N^C^N*-coordinating ligand and showed the interesting properties it gives to osmium(II) and ruthenium(II) complexes. Since then, this ligand turned out to have a rich coordination chemistry. For example, palladium (II) complexes bearing a *N^C^N* dpyb ligand are high-performance catalysts in the Heck reaction of iodobenzene and methyl acrylate, with a turnover frequency as high as 280 000 h^{-1} [10]. In addition, iridium(III) complexes bearing a *N^C^N*-1,3-di(2-pyridyl)-4,6-dimethylbenzene ligand (where the presence of the methyl groups block competitive cyclometallation at the C^4 and C^6 positions), in combination with *N^C* phenylpyridines, are bright emitters [11]. Due to their strong luminescence, many platinum(II) complexes of dipyridylbenzenes

found application in the organic light-emitting device (OLED) technology [12–16] and in biomedicine [17–21].

Thus, eight years after the pioneering work of Sauvage et al. on dpybH, Cardenas et al. observed that this pro-ligand reacts with K_2PtCl_4 in acetic acid, affording Pt(bpyb)Cl, the first Pt(II) complex with a cyclometallated *N^C^N* 1,3-bis(pyribin-2-yl)benzene ligand [22]. A few years thereafter, Williams et al. reported that this complex is a bright emitter at room temperature (Φ_{lum} = 0.60 and t = 7.2 ms in diluted deoxygenated dichloromethane solution) [23], due to the presence of a cyclometallating carbon and the rigidity of the *N^C^N* ligand [1]. An important aspect of these Pt(bpyb)Cl complexes is that the emission wavelength can be tuned by the donor/acceptor nature of the substituents on the pyridine and cyclometallating benzene. Thus, the presence of electron-donating substituents on the pyridine rings and/or electron-withdrawing groups on the benzene ring gives a blue-shifted emission, whereas the addition of electron-withdrawing groups in the pyridines and/or electron-donating groups in the benzene ring leads to a red-shifted one [24–26]. In addition, we recently reported that the introduction of a variously substituted phenyl or thienyl group in position 4 of the pyridine rings of the *N^C^N* 1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene ligand allows for the preparation of platinum(II) complexes with quantum yields approaching unity [27–29]; some of them already found application in the preparation of efficient OLEDs [27,29].

These observations, along with the known activity of triphenylethylene derivatives against estrogen receptor-positive breast cancer [30–32], the fascinating nature of tetraphenyethylene as a key component in dye-sensitized solar cells [33,34], and the great potential of both in luminogenic materials with aggregation-induced emission [35–39], prompted us to prepare 1,3-bis(4-triphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L1**, Figure 2) and 1,3-bis(4-tetraphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L2**). The related platinum(II) complexes (**1** and **2**) were also synthesized.

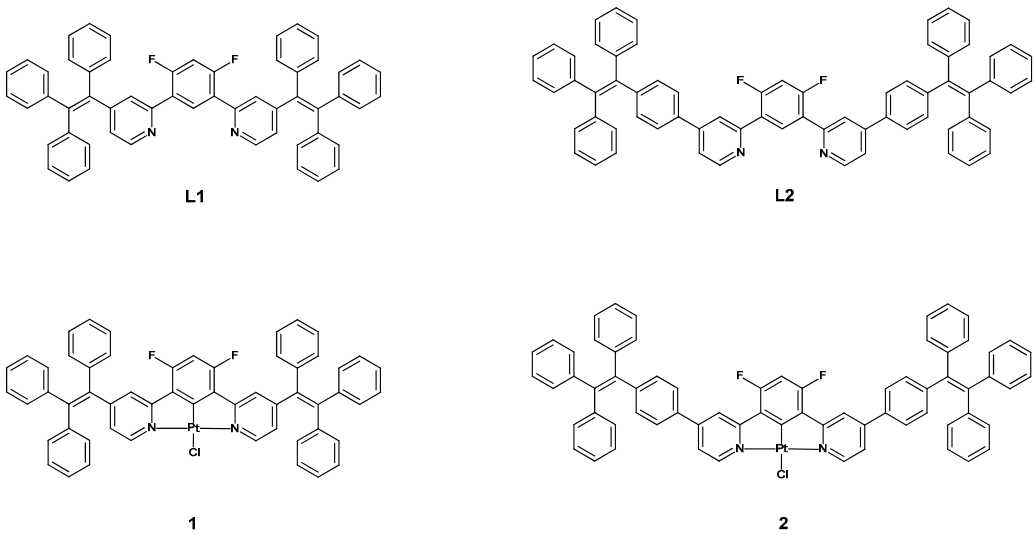


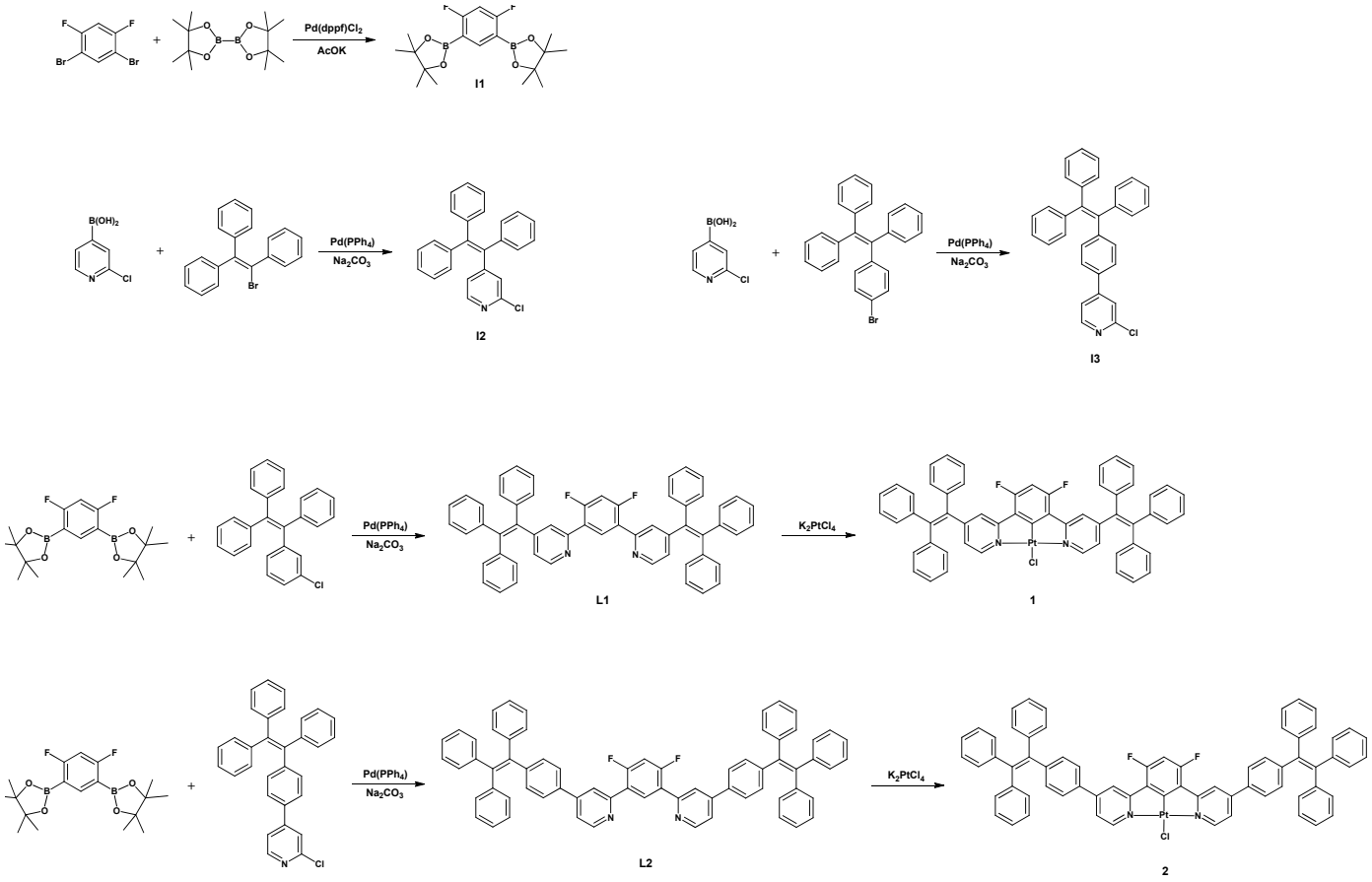
Figure 2. Chemical structure of the investigated compounds.

2. Results and Discussion

2.1. Synthesis of the Pro-Ligands and Related Platinum(II) Complexes

The new pro-ligands 1,3-bis(4-triphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L1**) and 1,3-bis(4-tetraphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L2**) are readily prepared by cross-coupling the pinacol ester of 1,3-difluoro-4,6-diboronic acid [40] with the suitable easily obtained 2-chloro-4-tri or tetra-phenylethylene-pyridine (Scheme 1, details of

the syntheses are given in the Supplementary Materials). Reaction of these pro-ligands with K_2PtCl_4 leads to the related **1** and **2** complexes. Pro-ligands and platinum(II) complexes were characterized by NMR spectroscopy, mass spectrometry and elemental analysis (see Supplementary Materials). Various attempts to obtain crystals of the platinum complexes suitable for X-ray structure determination failed. However, in agreement with the literature [27,28], and as expected upon cyclometallation of the pro-ligands with platinum, in the ^{1}H-NMR spectrum of the complexes, there is a loss of the signal corresponding to the proton of the benzene ring located between the two pyridines; as a consequence, the peak of the remaining protons on the benzene passes from a doublet to a singlet. Furthermore, the doublet signal associated with the protons in position 2 on the pyridines becomes shifted towards higher ppm (from 8.45 to 8.99 ppm) and undergoes coupling not only with the adjacent protons but also with the ^{195}Pt component of the metal, appearing as a couple of satellite peaks presenting a large ^{3}J of around 37 Hz (see Supplementary Materials). The formation of **1** and **2** was confirmed by high-resolution mass spectrometry and elemental analysis (see Supplementary Materials).



Scheme 1. Synthesis of pro-ligands **L1**–**L2** and related platinum(II) complexes **1**–**2**.

The new pro-ligands **L1** and **L2** open the doors for the preparation of *N^C^N* complexes with other metals. Specifically, they can be a springboard for the synthesis of novel thiocyanate-free ruthenium(II) photosensitizers for dye-sensitized solar cells (DSSCs). Up to now, the most commonly used photosensitizers had been the 2,2′-bipyridineruthenium(II) (2,2′-bipyridine = bpy) complexes with thiocyanate ancillary ligands that, however, can be easily replaced by other competing ligands present in the solar cell, yielding less efficient species [41,42]. Cyclometallated thiocyanate-free ruthenium complexes turned out to be a good alternative for DSSCs [43–49]. However, although cyclometallated *N^C^N* ruthe-

nium(II) complexes have been known since 1991 [6], to our knowledge, they have never been investigated as dyes in DSSCs. In addition, it has been reported that the introduction of a tetraphenylethylene moiety in both phenothiazine and porphyrin dyes is a way to suppress dye aggregation and charge recombination, leading to an enhancement of the photovoltages and efficiencies of DSSCs [33,34]. These observations suggest that ruthenium(II) complexes based on **L1** and **L2** could potentially be efficient dyes for DSSCs.

2.2. Photophysical Properties of the Platinum(II) Complexes

Complexes **1**–**2** were investigated from the photophysical point of view by recording their electronic absorption spectra in CH_2Cl_2 solution at room temperature and at different concentrations in order to calculate the molar extinction coefficients (ε) for the absorption maxima. As reported in Figure 3, both compounds show high intensity absorption bands below 330 nm ($\varepsilon_{244} = 5.6 \times 10^4$ M^{-1} cm^{-1} and $\varepsilon_{243} = 6.4 \times 10^4$ M^{-1} cm^{-1} for **1** and **2**, respectively), which are typically assigned to intraligand $^1\pi$–π^* transitions of the *N^C^N* ligand [50], whereas the metal to ligand charge transfer (MLCT) transitions occur in the 320–450 nm region ($\varepsilon_{391} = 3.1 \times 10^4$ M^{-1} cm^{-1} and $\varepsilon_{393} = 4.6 \times 10^4$ M^{-1} cm^{-1} for **1** and **2**, respectively), by analogy with other *N^C^N* platinum(II) complexes [50].

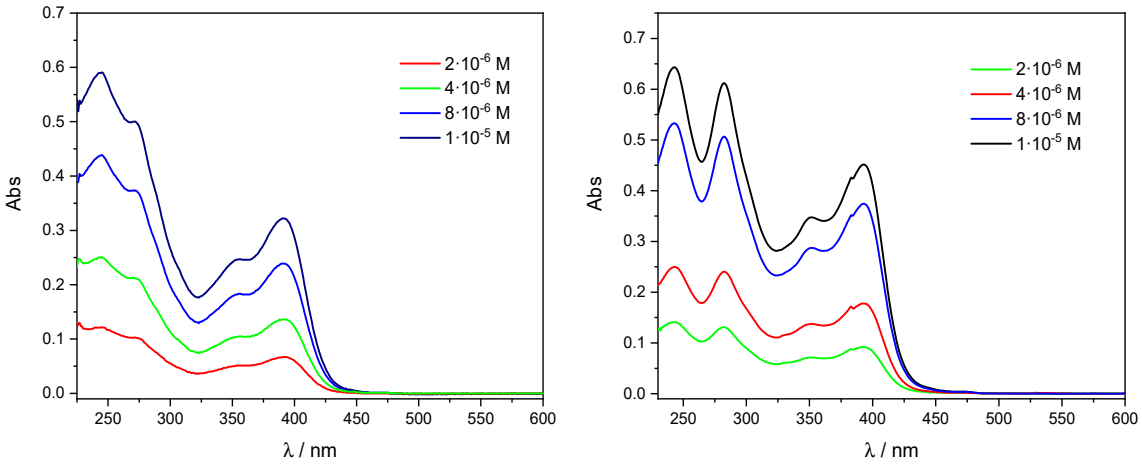


Figure 3. Absorption spectra of **1** (**left**) and **2** (**right**) in CH_2Cl_2 at different concentrations at 298 K.

Complexes **1** and **2** were studied from the luminescence point of view, registering their excitation and emission spectra and measuring their absolute Quantum Yield (QY) and lifetimes in a CH_2Cl_2 solution. Both complexes yielded very weak emission (maxima in the range 450–520 nm), with QY values in the range of 1.0–1.6% and excited-state lifetime of 5.73 and 4.82 μs for **1** and **2**, respectively, even after the Freeze-Pump-Thaw (FPT) procedure necessary to remove dissolved oxygen (Table 1). This poor luminescence is in agreement with the faint emission of tri- and tetra-phenylethylene in diluted solutions due to dynamic intramolecular rotations against the double bond of the phenyl groups [51–55]. Clearly, the rotational motions of the multiple peripheral phenyl rings likely remain active in the platinum complexes, thus favouring a high radiationless decay ($k_{nr} \approx 10^5$ s^{-1}) in the solution. Neither of the platinum complexes are emissive in the solid state, as powders, or when dispersed in a polymethyl methacrylate (PMMA) matrix (3% *w*/*w*). Complete photophysical data and spectra are reported in the Supplementary Materials (Figures S1–S4, Table S1).

We previously reported that the introduction of a variously substituted phenyl or thienyl group in position 4 of the pyridine rings of the *N^C^N* 1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene ligand allows for the preparation of platinum(II) complexes with quantum yields approaching unity [27–29]. In contrast, the results of the present work show that

the introduction of tri- and tetra-phenylethylene substituents on the pyridine rings is not a good strategy for the preparation of highly luminescent *N^C^N* platinum(II) complexes.

Table 1. Photophysical data for complexes **1** and **2** in CH_2Cl_2 solution. QY before (QY_{before}) and after (QY_{after}) Freeze-Pump-Thaw (FPT). Excited-state lifetime (τ) after FPT.

Complex	c/M	QY_{before} (QY_{after})	$\tau/\mu s$	$\lambda_{ex}, \lambda_{em}/nm$	[a] k_r/s^{-1}	[b] k_{nr}/s^{-1}
1	4×10^{-6}	1.4% (1.6%)	5.73	374, 512	2.79×10^3	1.72×10^5
2	4×10^{-6}	1.0% (1.2%)	4.82	368, 458	2.49×10^3	2.05×10^5

[a] $k_r = (QY)/\tau$; [b] $k_{nr} = (1 - QY)/\tau$.

3. Materials and Methods

Details on the synthesis of pro-ligands and related platinum(II) complexes are reported in the Supplementary Materials, along with their characterization (^1H, ^{13}C and ^{19}F NMR spectra, elemental analysis, mass spectrometry). Thin films were prepared via the spin-coating technique from CH_2Cl_2 solutions of PMMA (10% *w*/*w* with respect to the solvent) containing 3% *w*/*w* of the complex. Electronic absorption spectra were measured at room temperature in a CH_2Cl_2 solution, by means of a Shimadzu UV3600 spectrophotometer (Shimadzu Italia S.r.l., Milan, Italy) and quartz cuvettes (optical path length = 1 cm). Luminescence data were obtained in the CH_2Cl_2 solution after three Freeze-Pump-Thaw cycles, in order to remove dissolved oxygen. Absolute photoluminescence quantum yields (QY) were obtained with the C11347 Quantaurus Hamamatsu Photonics K.K spectrometer (Hamamatsu Photonics K.K., Hamamatsu, Japan). Steady-state and time-resolved fluorescence data were obtained by means of the FLS980 spectrofluorimeter (Edinburg Instrument Ltd., Livingston, UK). Measurement techniques are thoroughly described in the Supplementary Materials [56].

4. Conclusions

In conclusion, the two new *N^C^N* pro-ligands, namely 1,3-bis(4-triphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L1**) and 1,3-bis(4-tetraphenylethylene-pyridin-2-yl)-4,6-difluoro-benzene (**L2**), were prepared and thoroughly characterized along with their related platinum(II) complexes (**1** and **2**) which turned out to be poorly luminescent. In the near future, we plan to investigate the use of **L1** and **L2** as *N^C^N* pro-ligands in the preparation of thiocyanate-free ruthenium(II) sensitizers for dye-sensitized solar cells.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/inorganics14110281/s1. Synthesis and characterization of intermediates, pro-ligands and platinum(II) complexes; Photophysical characterization of **1** and **2** [56]; Figure S1: Excitation and emission spectra of complex **1** in CH_2Cl_2; Figure S2: Excitation and emission spectra of complex **2** in CH_2Cl_2; Figure S3: Excited-state decay of complex **1** in CH_2Cl_2 solution; Figure S4: Excited-state decay of complex **2** in CH_2Cl_2 solution; Table S1: Absorption maxima and corresponding molar extinction coefficients for complexes **1** and **2** in CH_2Cl_2 solution.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

dpybH	1,3-di(2-pyridyl)benzene
DSSC	dye-sensitized solar cell
$Pd(dppf)Cl_2$	[1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II)
ttpy	4′tolyl-2,2′:6′2″-terpyridine

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