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# Pincer-CNC mononuclear, dinuclear and heterodinuclear Au(III) and Pt(II) complexes supported by mono- and poly-N-heterocyclic carbenes: synthesis and photophysical properties†

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A family of cyclometallated Au(III) and Pt(II) complexes containing a CNC-pincer ligand (CNC = 2,6-diphenylpyridine) supported by pyrene-based mono- or bis-NHC ligands have been synthesized and characterized, together with the preparation of a Pt–Au hetero-dimetallic complex based on a Y-shaped tris-NHC ligand. The photophysical properties of all the new species and of two related Ru(II)–arene complexes were studied and compared. Whereas the pyrene-based complexes only exhibit emission in solution, those containing the Y-shaped tris-NHC ligand are only luminescent when dispersed in poly(methyl methacrylate) (PMMA). In particular, the pyrene-based complexes were found to be emissive in the range of 373–440 nm, with quantum yields ranging from 3.1 to 6.3%, and their emission spectra were found to be almost superimposable, pointing to the fluorescent pyrene-centered nature of the emission. This observation suggests that the emission properties of the pyrene fragment may be combined with some of the numerous applications of NHCs as supporting ligands allowing, for instance, the design of biological luminescent agents.

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## Introduction

During the last decade, the use of poly-N-heterocyclic carbene ligands has given access to a plethora of new polymetallic complexes whose properties often differ from their more closely related monometallic analogues.<sup>1</sup> While most of the applications of these polymetallic species have been explored in the field of homogeneous catalysis, where the presence of two or more metals has given clear evidence of activity improvement,<sup>2</sup> little has been done in other fields, such as the study of their potential photophysical applications, where the presence of two or more metals may also provide some benefits. Since the invention of luminescent organic devices in 1995,<sup>3</sup> there has been increasing interest in the development of materials with emissive properties, mostly due to the current interest in the

preparation of new optical devices and organic light emitting diodes (OLEDs). Most organic light emitters only show fluorescence,<sup>4</sup> and if triplet excitons are formed, they are often deactivated by thermal processes. A breakthrough in the preparation of this type of materials was the incorporation of transition metal complexes in 1998,<sup>5</sup> because the strong spin–orbit couplings introduced by the metal fragment allow fast energy transfer from the singlet to the triplet state to occur,<sup>6</sup> thus improving the efficiency of the OLED material. Although many transition metals have been investigated as emitting systems, iridium(III) and platinum(II) are those that have provided the best results thus far,<sup>7</sup> but ruthenium<sup>8</sup> and gold<sup>9</sup> have already shown very promising properties.<sup>10</sup> Normally, the presence of a chelating group is desirable for the preparation of metal complexes with good emitting properties, and the presence of an organic chromophore is usually required to impart the desired luminescence. For the choice of the cyclometallated ligands those featuring a combination of aryl and N-heterocyclic rings that bind through a partnership of C and N atoms are those that have been most extensively used. The incorporation of N-heterocyclic carbene ligands (NHCs) into metal-based luminescent materials has also provided significant benefits,<sup>10</sup> because NHCs are strong-field ligands that push the  $d\sigma^*$  orbitals to higher energy levels, thus non-radiative deactivation from these states may be inhibited to an important extent, an effect that is particularly important for highly

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electrophilic metals like Au(III).<sup>11</sup> Besides, NHCs provide stable complexes that facilitate the processability of the resulting emissive materials. In addition, pyrene has become one of the most widely studied organic materials in the field of photochemistry and photophysics,<sup>12</sup> and for this reason it has been the chromophore of choice in the design of many coordination complexes used in fields such as optoelectronics, chemical sensors and even photodynamic therapeutic agents.<sup>13</sup>

We recently reported the photophysical properties of a series of pyrene-containing azoliums and bisazoliums that showed emissions in the range of 370–420 nm, and quantum yields ranging from 0.29–0.75,<sup>14</sup> although their coordination to rhodium(I), iridium(I) and platinum(II) to afford the related NHC complexes provided materials with negligible emissive properties due to non-radiative deactivation.

Based on these preliminary results, herein we describe the preparation of new platinum(II) and gold(III) complexes containing a pyrene-bis-N-heterocyclic carbene ligand and a CNC-pincer ligand (CNC = 2,6-diphenylpyridine).<sup>15</sup> With the preparation of these complexes, we try to marry the benefits provided by the combined use of tridentate CNC ligands, NHCs and metal centers that can afford high emissive efficiencies. We also report the preparation of a Pt(II)–Au(III) hetero-dimetallic complex based on a Y-shaped tris-NHC ligand.<sup>16</sup> We considered this ligand an excellent support for the preparation of NHC-based mixed-metal complexes,<sup>2</sup> which may benefit from the combined properties of the metal fragments comprised in the heterometallic unit. An interesting example describing the preparation of a Au(I)–Ru(II) heterometallic complex was recently reported,<sup>17</sup> in which the photophysical properties provided by the ruthenium fragment are combined with the biological activity afforded by the gold unit.

## Results and discussion

### Synthesis and characterization

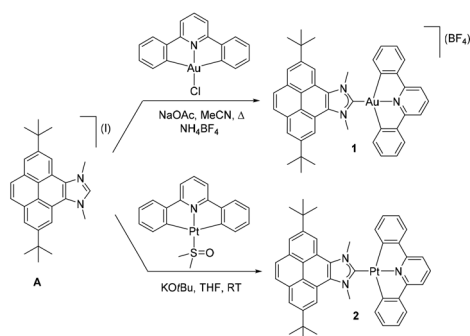
As depicted in Scheme 1, the mono-gold complex **1** was obtained by reaction of the pyrene-imidazolium iodide **A** with [Au(CNC)Cl] (CNC = 2,6-diphenylpyridine) in refluxing acetonitrile in the presence of NaOAc in high yield (90%). The reaction of **A** with [Pt(CNC)(DMSO)] in THF in the presence of

KOtBu led to the formation of the platinum complex **2** in 69% yield.

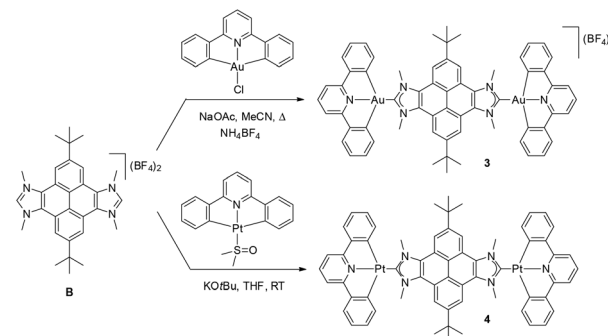
By following a similar protocol, but starting from the pyrene-bis-imidazolium salt **B**, the related di-gold and di-platinum complexes **3** and **4** were obtained in 81 and 77% yield, respectively (Scheme 2). The new complexes were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The <sup>1</sup>H NMR spectra of **1** and **2** confirm the twofold symmetry of both molecules due to the presence of a mirror plane, as exemplified by the equivalency of the protons of the methyl groups of the *tert*-butyl substituents, and the three resonances assigned to the six protons of the pyrene. The <sup>1</sup>H NMR spectra of **3** and **4** are fully consistent with the pseudo-*D*<sub>2h</sub> symmetry of the complexes, as illustrated by the equivalence of the aromatic protons of the pyrene and of the resonances corresponding to the CNC ligands. The <sup>13</sup>C NMR spectra of the complexes show the diagnostic signal assigned to the metalated carbene carbons, which appear at virtually identical chemical shifts for the two gold (164.0 ppm in **1**, 163.9 ppm in **3**) and platinum (179.5 ppm in **2**, 181.1 ppm in **4**) complexes.

The molecular structure of the di-platinum complex **4** was unambiguously confirmed by X-ray diffraction studies (Fig. 1). The molecule consists of two Pt(CNC) fragments, bound by the pyrene-bis-NHC ligand. The CNC bite angle is 161.2(2)°. The coordination planes of the two metal fragments are parallel, and deviate from the plane established by the pyrene unit by 69.46(15)°. The distance between the two metal atoms is 13.12 Å, and the Pt–C<sub>carbene</sub> bond distance is 1.972(5) Å.

For the preparation of a hetero-dimetallic Pt(II)–Au(III) complex, we decided to use our previously reported tris-imidazolium salt **C** (Scheme 3).<sup>16b</sup> As we already reported,<sup>16a</sup> the ligand can bind to two different metals by a stepwise procedure in which the first step invariably implies the coordination *via* the chelating side of the ligand, therefore facilitating the rational design of hetero-dimetallic complexes. This type of stepwise coordination of a ditopic ligand has also been successfully used by other authors for other types of polytopic NHC-based ligands,<sup>18</sup> although only in a few cases the stepwise metalation strategy is metal-selective,<sup>18c,e</sup> thus simplifying the access to heterometallic compounds. In this case we proceeded by the reaction of **C** with [Pt(C≡CPh)<sub>2</sub>(COD)] in

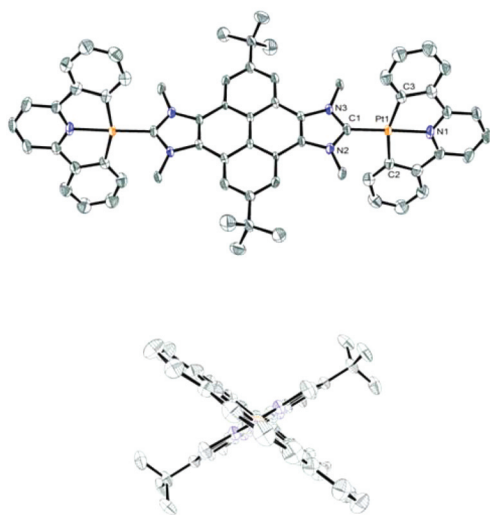


Scheme 1 Synthesis of complexes **1** and **2**.

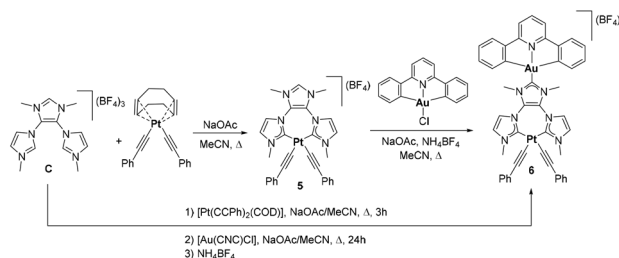


Scheme 2 Synthesis of complexes **3** and **4**.





**Fig. 1** Two perspectives of the molecular diagram of complex **4**. Hydrogen atoms and solvent ( $\text{CH}_2\text{Cl}_2$ ) have been omitted for clarity. Ellipsoids at the 50% probability level. Selected bond distances (Å) and bond angles ( $^\circ$ ): Pt(1)–C(1) 1.972(5), Pt(1)–N(1) 2.015(4), Pt(1)–C(3) 2.054(6), Pt(1)–C(2) 2.053(6), C(1)–Pt(1)–N(1) 178.5(2), C(1)–Pt(1)–C(3) 101.1(2), C(1)–Pt(1)–C(2) 97.7(2), N(1)–Pt(1)–C(3) 80.4(2), N(1)–Pt(1)–C(2) 80.8(2), C(2)–Pt(1)–C(3) 161.2(2).



**Scheme 3** Synthesis of complexes **5** and **6**.

refluxing acetonitrile, in the presence of NaOAc, which afforded the Pt(II) complex **5** in 74% yield. The second step of the synthesis involves the reaction of **5** with  $[\text{Au}(\text{CNC})\text{Cl}]$  and NaOAc, in refluxing acetonitrile, providing the hetero-dimetallic complex **6** in 18% yield. Interestingly, complex **6** can also be obtained by a one-pot procedure, by the sequential addition of  $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{COD})]$  and  $[\text{Au}(\text{CNC})\text{Cl}]$  over a solution of **C** in MeCN in the presence of NaOAc, as indicated in Scheme 3. In both synthetic procedures  $\text{NH}_4\text{BF}_4$  was added at the end of the process in order to facilitate the formation of the tetrafluoroborate salt of **6**. This stepwise synthesis of complex **6** is a new example that illustrates the easy access to hetero-dimetallic complexes by using the tris-imidazolium salt **C**. In this case, the preparation of **6** affords a good opportunity to study the photophysical properties of a dimetallic complex that combines the presence of two potentially active inorganic metal-based chromophores.

Compounds **5** and **6** were characterized by NMR spectroscopy and mass spectrometry. The electrospray MS spectrum

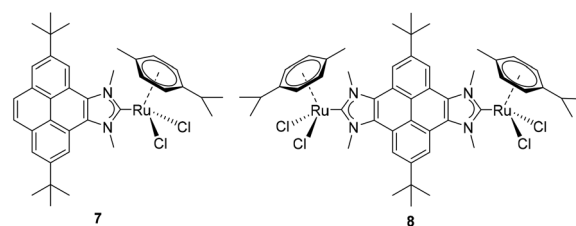
of **5** displayed a peak at  $m/z$  654.3 assigned to  $[\text{5-BF}_4]$ . The hetero-metallic nature of **6** could be ascertained by its electrospray mass spectrum, which displayed a peak at  $m/z$  1079.4, attributed to  $[\text{6-BF}_4]$ . The  $^1\text{H}$  NMR of **5** shows a singlet at  $\delta$  8.67, assigned to the NCHN proton of the remaining imidazolium ring. The  $^{13}\text{C}$  NMR of **5** shows the resonance corresponding to the two equivalent carbene carbons at 175.9 ppm. The  $^{13}\text{C}$  NMR signals due to the distinct carbene carbons in **6** appear at 175.7 and 165.5 ppm, for the Pt–C<sub>carbene</sub> and Au–C<sub>carbene</sub>, respectively.

### UV-Vis absorption and emission

The UV-visible absorption spectra of complexes **1–6** were studied in dichloromethane or acetonitrile at 298 K. We also included in our study the mono-ruthenium and di-ruthenium complexes **7** and **8** (Scheme 4),<sup>19</sup> and the azolium and bis-azolium salts **A** and **B**, for comparative purposes. The UV-Vis absorption spectra of the latter complexes were performed either in acetonitrile (**A** and **B**) or dichloromethane (**7** and **8**) at 298 K. All the photophysical data are summarized in Table 1.

The mono-NHC complexes **1**, **2** and **7** exhibit an intense absorption band between 246–255 nm. The bis-NHC complexes **3**, **4** and **8** show an intense absorption band between 236–262 nm. Complex **1**, as well as compounds **A** and **B**, exhibits a less intense vibronic-structured band at 310–340 nm, with vibronic spacings of 1488 and 1443  $\text{cm}^{-1}$ . These bands are assigned to pyrene-centered  $\pi$ – $\pi^*$  transitions.

The photoluminescence properties of the synthesized complexes were studied in solution and dispersed in poly(methyl methacrylate) (PMMA) films at 298 K. Upon excitation at  $\lambda = 310$  nm, degassed acetonitrile solutions of pyrene-based complexes **1–4**, **7** and **8** exhibit strong luminescence at 373–440 nm. Their emission spectra featured vibronically resolved bands, with peak maxima at 393 nm (Fig. S3–S6, S9 and S10†). In fact, the emission spectra of all the pyrene-based NHC complexes and salts **A** and **B** were superimposable. These similarities suggest that the exciton that forms in all these molecules is largely localized on the pyrene linker, with minimum participation of the heterocyclic fragments or the metals. Under the same conditions, complexes **5** and **6**, based on a Y-shaped tris-NHC ligand, were found to be non-emissive. These results may seem surprising, especially if we take into account the moderately intense luminescence ( $\Phi_f = 3.9 \times 10^{-3}$ ) shown by the gold(III) complex **9** (Scheme 5), which was originated from a metal perturbed  $^3[\pi \rightarrow \pi^*](\text{RC}^+\text{N}^-\text{CR})$  IL state, as



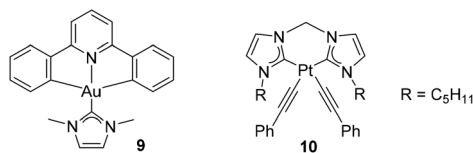
**Scheme 4** Ru(II) complexes **7** and **8**.



Table 1 Photophysical properties of A, B and 1–8

Entry	Comp.	$\lambda_{\text{abs}}$ (nm) ( $\log(\epsilon)^a$ )	$\lambda_{\text{em}}^d$ (nm)	$\tau^e$ (ns)	$\Phi_f^d$ (%)
1	A	251 (4.83), 277 (4.54), 307 (4.16), 321 (4.34), 336 (4.53) <sup>c</sup>	373, 393, 416, 440	78.8	32
2	B	263 (4.79), 274 (4.63), 286 (4.69), 307 (4.05), 320 (4.19), 335 (4.34) <sup>c</sup>	371, 391, 412, 436	43.1	41
3	1	246 (5.03), 281 (4.71), 325 (4.42), 341 (4.49) <sup>c</sup>	373, 393, 415, 437	8.5 (15%) 66.3 (85%)	6.3
4	2	255 (5.01), 304 (4.65), 352 (4.34) <sup>b</sup>	372, 392, 414, 437	6.5 (8%) 70.9 (92%)	3.5
5	3	236 (5.13), 281 (4.86), 293 (4.92), 344 (4.44), 379 (4.20) <sup>c</sup>	372, 392, 413, 437	3.8 (21%) 37.6 (79%)	3.6
6	4	257 (5.10), 305 (4.87), 348 (4.51), 394 (4.22) <sup>b</sup>	372, 392, 413, 437	3.2 (25%) 42.6 (75%)	3.1
7	5	257 (4.55), 305 (4.27) <sup>c</sup>	Not detected	—	[5.6] <sup>f</sup>
8	6	246 (4.57), 305 (4.16) <sup>c</sup>	Not detected	—	[0.9] <sup>f</sup>
9	7	255 (4.77), 293 (4.57), 302 (4.56), 348 (4.23) <sup>b</sup>	374, 394, 415, 440	8.1 (17%) 73.6 (83%)	3.2
10	8	262 (4.75), 300 (4.69), 356 (4.19), 385 (3.91) <sup>b</sup>	380, 394	6.5 (13%) 41.5 (87%)	4.5

<sup>a</sup> Molar extinction coefficients ( $\epsilon$ , in  $\text{M}^{-1} \text{cm}^{-1}$ ) were determined from Beer's law plots. <sup>b</sup> Measurements were performed in  $\text{CH}_2\text{Cl}_2$  under ambient conditions. <sup>c</sup> Measurements were performed in MeCN under ambient conditions. <sup>d</sup> Emission quantum yields were measured in degassed MeCN, with recrystallized anthracene in degassed EtOH as standard ( $\Phi_f = 0.278$ ),  $\lambda_{\text{exc}} = 310 \text{ nm}$ . <sup>e</sup> Measured in degassed MeCN,  $\lambda_{\text{exc}} = 304 \text{ nm}$ . <sup>f</sup> Values in brackets correspond to emission quantum yields recorded in PMMA films.



Scheme 5 Previously reported complexes 9 and 10.

previously published,<sup>20</sup> although non-emissive systems were also obtained by slight modifications of the NHC substituents. Similarly, the Pt(II) complexes **10** (Scheme 5) are known to exhibit emission at room temperature in  $\text{CH}_2\text{Cl}_2$ , although with low quantum yields ( $\Phi_f = 1\text{--}2 \times 10^{-3}$ ).<sup>21</sup>

The carbene coordination reduces but does not suppress the pyrene-centered emission of complexes **1–4**, **7** and **8** (compare entries 1 and 2 with 3–6, 9 and 10), suggesting that the carbene coordination to the Pt(II), Au(III) or Ru(II) center increases the proportion of non-radiative decay processes.<sup>22</sup> All in all the quantum yields referred to the pyrene-based NHC metal complexes range between 3.1–6.3%, which are rather high values compared to those shown by other complexes with the same pyrene-based bis-NHC ligands.<sup>14b</sup> This result is interesting, because it indicates that the emission properties of the pyrene fragment may be combined with the well-known antitumoral activity displayed by several gold and platinum complexes,<sup>23</sup> so that luminescent antitumoral agents may be accessible.

Emission lifetime measurements were performed using a nanosecond pulsed laser system in degassed acetonitrile. The excited-state lifetimes were found to be rather short, suggesting the fluorescent character of the luminescence for all metal complexes under study. The excited-state of complexes **1–8** exhibited bi-exponential decays, in which one long component (71–38 ns) with a larger contribution and a shorter one (3.2–8.5 ns) are present.

The emission quantum efficiencies were also recorded at 10 wt% (5 wt% for complexes **3** and **5** due to solubility issues) in PMMA films, exciting between 300 and 330 nm. Under these conditions, only the Y-shaped tris-NHC-based complexes **5** and **6** were found to be emissive, displaying quantum efficiencies of 5.6 and 0.9%, respectively (entries 7 and 8 in Table 1). In particular, complex **5** displays a vibronic-structured emission band between 415 and 600 nm with a band maximum at 430 nm (Fig. S11†). Complex **6** exhibits a less intense emission band between 475 and 575 nm with a band maximum at 517 nm (Fig. S12†), in line with the emission spectrum shown by **9**.<sup>20</sup>

## Electrochemistry

The electrochemical properties of complexes **1–6** were analysed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), in dichloromethane or acetonitrile using a 0.1 M solution of  $[\text{NBu}_4][\text{PF}_6]$  as the supporting electrolyte (Fig. S13–S19†). The cyclic voltammogram of the mono-gold complex **1** shows three irreversible reduction waves and no oxidation waves, which are assigned to the ligand-centered reduction of the CNC ligand.<sup>20,24</sup> Unfortunately, the cyclic voltammogram of the di-gold complex **3** could not be recorded due to its high insolubility.

The pyrene-based Pt(II) complexes **2** and **4** display a reversible and a quasi-reversible oxidation wave at 0.95 and 0.89 V, respectively, which can be attributed to a metal-centered redox process. In the case of the dimetallic complex **4**, the DPV analysis of the oxidation wave indicates the absence of electronic coupling between the two platinum centers, in agreement with the results observed for other bimetallic complexes linked by the same NHC-based polyaromatic ligand.<sup>14a,19</sup>

Complexes **5** and **6** displayed irreversible platinum-centered oxidation waves at 1.3 and 1.2 V, respectively. These highly





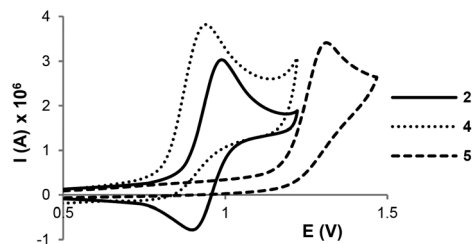


Fig. 2 CV plots of Pt(II)-based complexes **2**, **4** and **5** (1 mM in dry dichloromethane or acetonitrile with 0.1 M  $[\text{NBu}_4][\text{PF}_6]$  as the supporting electrolyte,  $\text{Fc}^+/\text{Fc}$  used as standard).  $50 \text{ mV s}^{-1}$  scan rate.

positive potentials may be attributed to the lower electron-donating character of the ligand, in combination with the cationic nature of the complexes (Fig. 2).

## Conclusions

In summary, in this work we prepared a series of pyrene-based monometallic and dimetallic complexes with pincer-CNC Au(III) and Pt(II) fragments. Additionally, based on a Y-shaped tris-NHC ligand, we prepared a Pt–Au hetero-dimetallic complex, together with a monometallic Pt(II) complex. These two complexes display the Pt(II) fragment at the chelating part of the ligand. The hetero-dimetallic complex contains a Au(III) fragment with a pincer CNC ligand bound to the mono-NHC part of the Y-shaped tris-NHC. The preparation of the Pt(II)/Au(III) hetero-dimetallic complex constitutes a novel example of the easy access to heterometallic complexes using our previously reported Y-shaped tris-NHC. While our initial interest in obtaining heterometallic complexes was based on their use for homogeneously catalyzed tandem processes, in this case we aimed to determine the influence of combining with potentially emissive fragments on the luminescence properties of the resulting complex.

The study of the emissive properties of the pyrene-based metal complexes in solution showed that they displayed moderate pyrene-centered emissions, although with significant lower efficiencies compared to their related mother ligands. The same complexes are non-emissive in the solid state, probably due to molecular aggregation (such as  $\pi$ – $\pi$  stacking interactions).

On the other hand, the two complexes based on the Y-shaped ligand are emissive in the solid state, but non-emissive in solution. By comparing the solid state emissions, it can be concluded that for the two complexes the emission is centered on the Pt(II) fragment.

Our results did not fully accomplish our initial objectives, which aimed to provide homo- and hetero-dimetallic complexes with enhanced luminescence properties compared to their monometallic analogues, but we believe that we established a wide-open pathway for the exploration of new families of multimetallic complexes with great photophysical potential. Our lab is currently searching for the preparation of hetero-

dimetallic complexes in which the properties of the two different metal fragments are combined in order to afford new materials with enhanced luminescence properties.

## Experimental

### General methods

The metal complexes  $[\text{Au}(\text{CNC})\text{Cl}]$ ,<sup>25</sup>  $[\text{Pt}(\text{CNC})\text{DMSO}]$ ,<sup>26</sup> and  $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{COD})]$ <sup>27</sup> were prepared according to literature methods. The imidazolium salts **A**,<sup>19</sup> **B**<sup>14a</sup> and **C**<sup>16b</sup> were previously reported by us, as well as the ruthenium based complexes **7** and **8**.<sup>19</sup> All operations were carried out by using standard Schlenk tube techniques under a nitrogen atmosphere unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased from Aldrich and degassed prior to use by purging with nitrogen and kept over molecular sieves. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Inova 300 and 500 MHz, using  $\text{CDCl}_3$ ,  $\text{CD}_3\text{CN}$  or  $\text{DMSO}-d_6$  as solvents. Electrospray mass spectra (ESI-MS) were recorded on a Micro-mass Quattro LC instrument; nitrogen was employed as drying and nebulizing gas. Exact mass analysis was realized using a Q-TOF Premier mass spectrometer with an electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16 000 (FWHM). Elemental analyses were carried out on a EuroEA3000 EuroVector Analyzer. Infrared spectra (FTIR) were obtained on a Bruker EQUINOX 55 spectrometer with a spectral window of  $4000\text{--}600 \text{ cm}^{-1}$ .

### General spectroscopic considerations

UV-visible absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer using  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  as a solvent, under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog®-3 spectrofluorometer employing degassed  $\text{CH}_3\text{CN}$ . Extinction coefficients ( $\epsilon$ ) were determined from Beer's law measurements using solutions with the concentration of the analyte of 10, 20, 30 and  $40 \mu\text{M}$  or 10, 15, 20 and  $25 \mu\text{M}$ . Quantum yields in solution were determined relative to recrystallized anthracene in degassed EtOH as a standard ( $\Phi_f = 0.27$ ),<sup>28</sup> exciting at 317 nm. All solutions were prepared in air and de-aerated by sparging with nitrogen for 20 min prior to performing emission and quantum yield measurements. Time-resolved fluorescence measurements were performed using time-correlated single-photon counting (TCSPC) on the Horiba Jobin-Yvon IBH-5000U. The samples were excited using a 304 nm NanoLED with a FWHM of 1.3 ns at a repetition ratio of 100 kHz. Signals were collected by using an IBH Data Station Hub photon-counting module. The quality of the fit was assessed by minimizing the reduced chi ( $\chi^2$ ) squared function and visual inspection of the weighted residuals. Direct quantum yield measurements were performed for solid samples at room temperature in a Hamamatsu absolute PL quantum yield spectrometer C11347.



## Electrochemistry

Electrochemical studies were carried out by using an Autolab Potentiostat, Model PGSTAT101 using a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver wire reference electrode. In all experiments,  $[\text{NBu}_4][\text{PF}_6]$  (0.1 M in dry  $\text{CH}_2\text{Cl}_2$  or MeCN) was used as the supporting electrolyte with an analyte concentration of approximately 1 mM. Measurements were performed at 50 mV  $\text{s}^{-1}$  scan rate. All redox potentials were referenced to the  $\text{Fc}^+/\text{Fc}$  couple as an internal standard with  $E_{1/2}(\text{Fc}/\text{Fc}^+)$  vs. SCE = +0.46 V.<sup>29</sup>

**Synthesis of 1.** A mixture of compound **A** (58.4 mg, 0.115 mmol),  $[\text{Au}(\text{CNC})\text{Cl}]$  (50 mg, 0.108 mmol) and NaOAc (18.9 mg, 0.23 mmol) in acetonitrile (30 mL) was refluxed overnight. Then, at room temperature,  $\text{NH}_4\text{BF}_4$  (121.2 mg, 1.08 mmol) was added and the mixture was stirred for 2 h. The solvent was removed under vacuum. The yellowish solid residue was suspended in  $\text{CH}_2\text{Cl}_2$ , and filtered to remove insoluble inorganic salts. Precipitation of the filtrate with a mixture of  $\text{CH}_2\text{Cl}_2$ /diethyl ether afforded compound **1** as a yellow solid. Yield: 87.2 mg, 90%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.99 (d,  $^4J_{\text{H-H}} = 1.5$  Hz, 2H,  $\text{CH}_{\text{pyrene}}$ ), 8.54 (d,  $^4J_{\text{H-H}} = 1.5$  Hz, 2H,  $\text{CH}_{\text{pyrene}}$ ), 8.33 (t,  $^3J_{\text{H-H}} = 8.0$  Hz, 1H,  $\text{CH}_{\text{pyridyl}}$ ), 8.31 (s, 2H,  $\text{CH}_{\text{pyrene}}$ ), 8.13 (d,  $^3J_{\text{H-H}} = 8.0$  Hz, 2H,  $\text{CH}_{\text{pyridyl}}$ ), 8.05 (d,  $^3J_{\text{H-H}} = 7.7$  Hz, 2H,  $\text{CH}_{\text{phenyl}}$ ), 7.38 (td,  $J = 7.2, 2.3$  Hz, 2H,  $\text{CH}_{\text{phenyl}}$ ), 7.23 (t,  $^3J_{\text{H-H}} = 9.2$  Hz, 2H,  $\text{CH}_{\text{phenyl}}$ ), 7.22 (m, 2H,  $\text{CH}_{\text{phenyl}}$ ), 4.83 (s, 6H,  $\text{NCH}_3$ ), 1.62 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  164.0 (Au-C<sub>carbene</sub>), 163.8 ( $\text{C}_q$  CNC), 159.2 ( $\text{C}_q$  CNC), 149.8 ( $\text{C}_q$  CNC), 149.0 ( $\text{C}_q$  pyrene), 144.5 ( $\text{CH}_{\text{pyridyl}}$ ), 135.9 ( $\text{CH}_{\text{phenyl}}$ ), 132.1 ( $\text{CH}_{\text{phenyl}}$ ), 131.32 ( $\text{C}_q$  pyrene), 129.20 ( $\text{C}_q$  pyrene), 128.2 ( $\text{CH}_{\text{pyrene}}$ ), 127.7 ( $\text{CH}_{\text{phenyl}}$ ), 126.7 ( $\text{CH}_{\text{phenyl}}$ ), 123.5 ( $\text{CH}_{\text{pyrene}}$ ), 120.7 ( $\text{C}_q$  pyrene), 120.4 ( $\text{C}_q$  pyrene), 118.6 ( $\text{CH}_{\text{pyridyl}}$ ), 117.2 ( $\text{CH}_{\text{pyrene}}$ ), 40.4 ( $\text{NCH}_3$ ), 35.3 ( $\text{C}(\text{CH}_3)_3$ ), 31.5 ( $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{AuN}_3\text{C}_{44}\text{H}_{41}\text{BF}_4 \cdot (\text{H}_2\text{O})_5$  (985.35): C, 53.61; H, 5.22; N, 4.26. Found: C, 53.40; H, 3.84; N, 3.99. Electrospray MS (20 V,  $m/z$ ): 808.4  $[\text{M}]^+$ .

**Synthesis of 2.** A mixture of compound **A** (50.6 mg, 0.099 mmol),  $[\text{Pt}(\text{CNC})\text{DMSO}]$  (50 mg, 0.099 mmol) and  $\text{KOtBu}$  (12.9 mg, 0.11 mmol) in THF (20 mL) was stirred at room temperature overnight. Then, the solvent was removed under vacuum. The yellowish solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered. Precipitation with a mixture of  $\text{CH}_2\text{Cl}_2$ /MeOH afforded compound **2** as a yellow solid. Yield: 55.6 mg, 69%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94 (s, 2H,  $\text{CH}_{\text{pyr}}$ ), 8.24 (s, 2H,  $\text{CH}_{\text{pyr}}$ ), 8.10 (s, 2H,  $\text{CH}_{\text{pyr}}$ ), 7.65 (t,  $^3J_{\text{H-H}} = 7.9$  Hz, 1H,  $\text{CH}_{\text{pyridyl}}$ ), 7.54 (d,  $^3J_{\text{H-H}} = 7.1$  Hz, 2H,  $\text{CH}_{\text{phenyl}}$ ), 7.38 (d,  $^3J_{\text{H-H}} = 7.9$  Hz, 2H,  $\text{CH}_{\text{pyridyl}}$ ), 7.16 (d,  $^3J_{\text{H-H}} = 6.3$  Hz, 2H,  $\text{CH}_{\text{phenyl}}$ ), 7.08–6.98 (m, 4H,  $\text{CH}_{\text{phenyl}}$ ), 4.82 (s, 6H,  $\text{NCH}_3$ ), 1.62 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  179.5 (Pt-C<sub>carbene</sub>), 169.3 ( $\text{C}_q$  CNC), 166.9 ( $\text{C}_q$  CNC), 150.6 ( $\text{C}_q$  CNC), 149.0 ( $\text{C}_q$  pyrene), 139.6 ( $\text{CH}_{\text{pyridyl}}$ ), 138.6 ( $^2J_{\text{Pt-C}} = 71$  Hz,  $\text{CH}_{\text{phenyl}}$ ), 132.0 ( $\text{C}_q$  pyrene), 130.6 ( $^3J_{\text{Pt-C}} = 39$  Hz,  $\text{CH}_{\text{phenyl}}$ ), 129.0 ( $\text{C}_q$  pyrene), 128.4 ( $\text{CH}_{\text{pyrene}}$ ), 124.3 ( $^3J_{\text{Pt-C}} = 25.5$  Hz,  $\text{CH}_{\text{phenyl}}$ ), 123.4 ( $\text{CH}_{\text{phenyl}}$ ), 122.1 ( $\text{CH}_{\text{pyrene}}$ ), 121.7 ( $\text{C}_q$  pyrene), 121.1 ( $\text{C}_q$  pyrene), 116.2 ( $\text{CH}_{\text{pyrene}}$ ), 114.8 ( $^3J_{\text{Pt-C}} = 24.8$  Hz,  $\text{CH}_{\text{pyridyl}}$ ), 40.7 ( $^3J_{\text{Pt-C}} = 64.5$  Hz,  $\text{NCH}_3$ ), 35.6 ( $\text{C}(\text{CH}_3)_3$ ), 32.1

( $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{PtN}_3\text{C}_{44}\text{H}_{41} \cdot (\text{H}_2\text{O})_4$  (878.33): C, 60.12; H, 5.62; N, 4.78. Found: C, 59.63; H, 5.83; N, 4.46. Electrospray MS (20 V,  $m/z$ ): 807.3  $[\text{M} + \text{H}]^+$ .

**Synthesis of 3.** A mixture of compound **B** (35.7 mg, 0.057 mmol),  $[\text{Au}(\text{CNC})\text{Cl}]$  (50 mg, 0.108 mmol) and NaOAc (18.9 mg, 0.23 mmol) in acetonitrile (30 mL) was refluxed overnight. Then, at room temperature,  $\text{NH}_4\text{BF}_4$  (121.2 mg, 1.08 mmol) was added and the mixture was stirred for 2 h. The solvent was reduced under vacuum and the product was precipitated with diethyl ether. The solid was recovered by filtration, washed with water several times, then with diethyl ether and dried under vacuum, yielding compound **3** as a yellow solid. Yield: 68.7 mg, 81%.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.18 (s, 4H,  $\text{CH}_{\text{pyr}}$ ), 8.34 (t,  $^3J_{\text{H-H}} = 8.0$  Hz, 2H,  $\text{CH}_{\text{pyridyl}}$ ), 8.15 (d,  $^3J_{\text{H-H}} = 8.0$  Hz, 4H,  $\text{CH}_{\text{pyridyl}}$ ), 8.07 (d,  $^3J_{\text{H-H}} = 7.8$  Hz, 4H,  $\text{CH}_{\text{phenyl}}$ ), 7.41 (t,  $^3J_{\text{H-H}} = 7.1$  Hz, 4H,  $\text{CH}_{\text{phenyl}}$ ), 7.26 (m, 8H,  $\text{CH}_{\text{phenyl}}$ ), 4.91 (s, 12H,  $\text{NCH}_3$ ), 1.68 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  163.9 (Au-C<sub>carbene</sub>), 163.8 ( $\text{C}_q$  CNC), 160.9 ( $\text{C}_q$  CNC), 149.8 ( $\text{C}_q$  CNC), 149.6 ( $\text{C}_q$  pyrene), 144.5 ( $\text{CH}_{\text{pyridyl}}$ ), 136.0 ( $\text{CH}_{\text{phenyl}}$ ), 132.1 ( $\text{CH}_{\text{phenyl}}$ ), 129.3 ( $\text{C}_q$  pyrene), 127.7 ( $\text{CH}_{\text{phenyl}}$ ), 126.7 ( $\text{CH}_{\text{phenyl}}$ ), 121.3 ( $\text{C}_q$  pyrene), 119.4 ( $\text{C}_q$  pyrene), 118.7 ( $\text{CH}_{\text{pyridyl}}$ ), 118.0 ( $\text{CH}_{\text{pyrene}}$ ), 40.8 ( $\text{NCH}_3$ ), 35.7 ( $\text{C}(\text{CH}_3)_3$ ), 31.3 ( $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{Au}_2\text{N}_6\text{C}_{64}\text{H}_{56}\text{B}_2\text{F}_8 \cdot (\text{H}_2\text{O})_5$  (1566.45): C, 49.06; H, 4.25; N, 5.37. Found: C, 49.05; H, 4.01; N, 5.14. Electrospray MS (20 V,  $m/z$ ): 651.3  $[\text{M}]^{2+}$ .

**Synthesis of 4.** A mixture of compound **B** (31.1 mg, 0.05 mmol),  $[\text{Pt}(\text{CNC})\text{DMSO}]$  (50 mg, 0.099 mmol) and  $\text{KOtBu}$  (12.9 mg, 0.11 mmol) in THF (20 mL) was stirred at room temperature overnight. Then, the solvent was removed under vacuum. The yellowish solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered. Precipitation with a mixture of  $\text{CH}_2\text{Cl}_2$ /pentane afforded compound **4** as a yellow solid. Yield: 49 mg, 77%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.04 (s, 4H,  $\text{CH}_{\text{pyrene}}$ ), 7.67 (t,  $^3J_{\text{H-H}} = 7.9$  Hz, 2H,  $\text{CH}_{\text{pyridyl}}$ ), 7.60–7.49 (m, 4H,  $\text{CH}_{\text{phenyl}}$ ), 7.40 (d,  $^3J_{\text{H-H}} = 7.9$  Hz, 4H,  $\text{CH}_{\text{pyridyl}}$ ), 7.24–7.17 (m, 4H,  $\text{CH}_{\text{phenyl}}$ ), 7.07 (m, 4H,  $\text{CH}_{\text{phenyl}}$ ), 4.88 (s, 12H,  $\text{NCH}_3$ ), 1.66 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  181.1 (Pt-C<sub>carbene</sub>), 169.3 ( $^1J_{\text{Pt-C}} = 695$  Hz,  $\text{C}_q$  CNC), 166.9 ( $^2J_{\text{Pt-C}} = 64.5$  Hz,  $\text{C}_q$  CNC), 150.6 ( $^2J_{\text{Pt-C}} = 30.7$ ,  $\text{C}_q$  CNC), 149.2 ( $\text{C}_q$  pyrene), 139.7 ( $\text{CH}_{\text{pyridyl}}$ ), 138.5 ( $^2J_{\text{Pt-C}} = 69$  Hz,  $\text{CH}_{\text{phenyl}}$ ), 130.6 ( $^3J_{\text{Pt-C}} = 38$  Hz,  $\text{CH}_{\text{phenyl}}$ ), 129.2 ( $\text{C}_q$  pyrene), 124.4 ( $^3J_{\text{Pt-C}} = 24$  Hz,  $\text{CH}_{\text{phenyl}}$ ), 123.5 ( $\text{CH}_{\text{phenyl}}$ ), 122.4 ( $\text{C}_q$  pyrene), 118.9 ( $\text{C}_q$  pyrene), 115.6 ( $\text{CH}_{\text{pyrene}}$ ), 114.9 ( $^3J_{\text{Pt-C}} = 24$  Hz,  $\text{CH}_{\text{pyridyl}}$ ), 41.1 ( $^3J_{\text{Pt-C}} = 75$  Hz,  $\text{NCH}_3$ ), 35.9 ( $\text{C}(\text{CH}_3)_3$ ), 32.0 ( $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{Pt}_2\text{N}_6\text{C}_{64}\text{H}_{56} \cdot (\text{H}_2\text{O})_2$  (1334.41): C, 57.56; H, 4.53; N, 6.29. Found: C, 57.48; H, 4.24; N, 5.81. Electrospray MS (20 V,  $m/z$ ): 1299.4  $[\text{M} + \text{H}]^+$ .

**Synthesis of 5.** A mixture of compound **C** (50 mg, 0.096 mmol),  $[\text{Pt}(\text{CCPh})_2(\text{COD})]$  (48.6 mg, 0.096 mmol) and NaOAc (31.6 mg, 0.38 mmol) in acetonitrile (15 mL) was refluxed for three hours. The mixture was then filtered at 0 °C and the solution was concentrated under reduced pressure. After addition of diethyl ether, compound **5** precipitated as a brownish solid which was collected by filtration and washed with diethyl ether. Yield: 52.8 mg, 74%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.67 (s, 1H,  $\text{NCHN}$ ), 7.49 (d,  $^3J_{\text{H-H}} = 2.2$  Hz, 2H,  $\text{CH}_{\text{imid}}$ ), 7.35 (d,  $^3J_{\text{H-H}} = 2.2$  Hz, 2H,  $\text{CH}_{\text{imid}}$ ), 7.16 (m, 10H,



$\text{CH}_{\text{phenyl}}$ ), 4.06 (s, 6H,  $\text{NCH}_3$ ), 3.88 (s, 6H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  175.9 (Pt- $\text{C}_{\text{carbene}}$ ), 135.0 ( $\text{NCHN}$ ), 131.6 ( $\text{CH}_{\text{phenyl}}$ ), 129.9 ( $\text{C}_q$ ), 129.0 ( $\text{CH}_{\text{phenyl}}$ ), 126.3 ( $\text{CH}_{\text{imid}}$ ), 125.8 ( $\text{CH}_{\text{phenyl}}$ ), 125.2 ( $\text{C}_q$ ), 121.2 ( $\text{CH}_{\text{imid}}$ ), 108.0 (Pt- $\text{C}\equiv\text{C}$ ), 106.1 (Pt- $\text{C}\equiv\text{C}$ ), 39.4 ( $\text{NCH}_3$ ), 35.8 ( $\text{NCH}_3$ ). Anal. Calc. for  $\text{PtN}_6\text{C}_{29}\text{H}_{27}\text{BF}_4$  (741.20): C, 46.97; H, 3.67; N, 11.34. Found: C, 46.53; H, 3.63; N, 11.29. Electrospray MS (20 V,  $m/z$ ): 654.3  $[\text{M}]^+$ .

**Synthesis of 6.** A mixture of compound C (50 mg, 0.096 mmol),  $[\text{Pt}(\text{CCPh})_2(\text{COD})]$  (48.6 mg, 0.096 mmol) and NaOAc (31.6 mg, 0.38 mmol) in acetonitrile (20 mL) was refluxed for three hours.  $[\text{Au}(\text{CNC})\text{Cl}]$  (44.5 mg, 0.096 mmol) and NaOAc (16 mg, 0.193 mmol) were then added and the resulting mixture was refluxed for 24 hours. Afterwards, at room temperature,  $\text{NH}_4\text{BF}_4$  (108 mg, 0.96 mmol) was added and the reaction mixture was stirred for 2 h. The mixture was filtered through a pad of Celite and the solvent was removed under vacuum. The crude solid was purified by column chromatography. Elution using mixtures of  $\text{CH}_2\text{Cl}_2/\text{acetone}$  (from 7:3 to 1:1) afforded the separation of an orange band which contained compound 6. Precipitation with a mixture of acetonitrile/diethyl ether gave the desired product as a brownish solid. Yield: 20 mg, 18%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.16 (t,  $^3J_{\text{H-H}} = 8.0$  Hz, 1H,  $\text{CH}_{\text{pyridyl}}$ ), 7.86–7.81 (m, 4H,  $\text{CH}_{\text{pyridyl}}$ ,  $\text{CH}_{\text{phenyl}}$ ), 7.64 (d,  $^3J_{\text{H-H}} = 2.1$  Hz, 2H,  $\text{CH}_{\text{imid}}$ ), 7.44–7.31 (m, 9H,  $\text{CH}_{\text{phenyl}}$ ,  $\text{CH}_{\text{imid}}$ ), 7.23–7.17 (m, 7H,  $\text{CH}_{\text{phenyl}}$ ), 7.11–7.07 (m, 2H,  $\text{CH}_{\text{phenyl}}$ ), 4.10 (s, 6H,  $\text{NCH}_3$ ), 3.87 (s, 6H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  175.7 (Pt- $\text{C}_{\text{carbene}}$ ), 165.5 (Au- $\text{C}_{\text{carbene}}$ ), 165.5 ( $\text{C}_q$  CNC), 164.8 ( $\text{C}_q$  CNC), 164.6 ( $\text{C}_q$  CNC), 153.5 ( $\text{C}_q$  CNC), 150.8 ( $\text{C}_q$  CNC), 150.8 ( $\text{C}_q$  CNC), 145.5 (CH), 137.4 (CH), 136.9 (CH), 133.4 (CH), 133.3 (CH), 131.6 (CH), 130.1 ( $\text{C}_q$ ), 129.1 (CH), 129.0 (CH), 127.7 (CH), 127.6 (CH), 126.5 (CH), 126.0 ( $\text{CH}_{\text{imid}}$ ), 125.7 (CH), 121.5 ( $\text{CH}_{\text{imid}}$ ), 119.5 (CH), 119.4 (CH), 118.0 ( $\text{C}_q$ ), 107.9 (Pt- $\text{C}\equiv\text{C}$ ), 106.5 (Pt- $\text{C}\equiv\text{C}$ ), 39.3 ( $\text{NCH}_3$ ), 37.8 ( $\text{NCH}_3$ ). Slow decomposition of the complex prevented a correct elemental analysis. Electrospray MS (20 V,  $m/z$ ): 1079.4  $[\text{M}]^+$ .

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