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# Selective synthesis, reactivity and luminescence of unsymmetrical bis-cyclometalated Pt(IV) complexes

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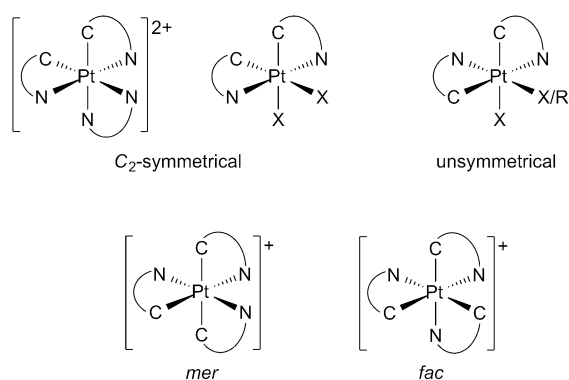
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† Electronic supplementary information (ESI) available: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of new compounds, crystallographic information, and computational data. CCDC 1913448 (**2af**), 1913449 (**2ed**), 1913450 (**3af**), 1913451 (**3bd**), 1913452 (**3cd**), 1913453 (**4-Et<sub>2</sub>O**), and 1913441 (**6-0.5CH<sub>2</sub>Cl<sub>2</sub>**). For ESI and crystallographic data in CIF format see DOI: 10.1039/x0xx00000x

Pt(II) complexes *cis-N,N*-[PtCl(C<sup>^</sup>N)(N<sup>^</sup>C<sup>^</sup>H)], where C<sup>^</sup>N represents a monocyclometalated 2,6-diaryl- or 2-arylpyridine ligand and N<sup>^</sup>C<sup>^</sup>H is an *N*-coordinated 2-arylpyridine, are selectively obtained from bridge-cleavage reactions of dimers [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(C<sup>^</sup>N)<sub>2</sub>] with excess of N<sup>^</sup>C<sup>^</sup>H at room temperature; isolation and characterization of derivatives of this kind is reported for the first time. Oxidation with PhICl<sub>2</sub> affords Pt(IV) complexes [PtCl<sub>2</sub>(C<sup>^</sup>N)(C<sup>^</sup>N<sup>^</sup>)], bearing two cyclometalated ligands in an unsymmetrical arrangement. The abstraction of the two chlorides using AgOTf at 120 °C in the presence of an additional 2-arylpyridine ligand leads to *mer* isomers of tris-cyclometalated Pt(IV) complexes if C<sup>^</sup>N derives from a 2-arylpyridine, whereas it results in a reductive C–C coupling if C<sup>^</sup>N is a monocyclometalated 2,6-diarylpyridine. Complexes [PtCl<sub>2</sub>(C<sup>^</sup>N)(C<sup>^</sup>N<sup>^</sup>)] show phosphorescence in frozen PrCN glasses arising from essentially <sup>3</sup>LC excited states localized on the cyclometalated ligand with the lowest π-π\* transition energy. The combined photophysical data and computational results substantiate a variable degree of MLCT admixture into the emitting state depending on the atom trans to the metalated carbon of the chromophoric ligand (Cl or N), which has an appreciable effect on the characteristics of the observed luminescence.

## Introduction

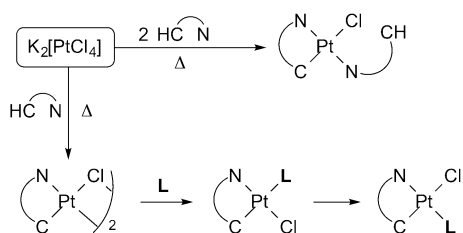
The synthesis and photophysical properties of late transition-metal complexes with chelating heteroaromatic ligands have been the subject of intensive research owing to the wide applicability of their long-lived excited states, including the development of electrophosphorescent materials,<sup>1,2</sup> chemical and biological sensors,<sup>3–5</sup> photocatalysts,<sup>6,7</sup> and photosensitizers in photodynamic therapy.<sup>8,9</sup> The use of cyclometalated 2-arylpyridines (C<sup>^</sup>N) and related ligands has proved particularly fruitful, because it has allowed to obtain complexes with broad colour-tuning possibilities and high emission efficiencies, most often with the Ir(III)<sup>10</sup> and Pt(II)<sup>11–13</sup> ions. Pt(IV) complexes bearing cyclometalated heteroaromatic ligands are still relatively scarce and only very recently has their potential as efficient phosphorescent emitters begun to be uncovered.<sup>14</sup> The reported phosphorescent Pt(IV) complexes of this class may combine two cyclometalated C<sup>^</sup>N ligands in a C<sub>2</sub>-symmetrical or unsymmetrical arrangement with diverse neutral or anionic ancillary ligands,<sup>15–22</sup> or contain three C<sup>^</sup>N ligands in a meridional (*mer*) or facial (*fac*) configuration<sup>14,23,24</sup> (Chart 1). In addition, luminescent Pt(IV) complexes bearing cyclometalated aryl-*N*-heterocyclic carbene and bi- or terdentate 2,6-diarylpyridine ligands have been recently reported by us.<sup>25</sup>



**Chart 1.** Structural types of phosphorescent cyclometalated Pt(IV) complexes. C<sup>N</sup> = cyclometalated 2-arylpyridine. X = halide or carboxylate. R = alkyl or C<sub>6</sub>F<sub>5</sub>. N<sup>N</sup> = aromatic diimine.

The phosphorescence of cyclometalated Pt(IV) complexes usually arises from triplet ligand-centred (<sup>3</sup>LC or <sup>3</sup>π-π\*) excited states mainly localized on the C<sup>N</sup> ligands with a very small but critical metal-to-ligand charge-transfer (MLCT) character mixed in. Emission lifetimes are typically very long (from tens to hundreds of microseconds), which make them interesting candidates for applications that benefit from long-lived excited states, such as photosensitizing, photocatalysis or chemosensing. The development of colour-tunable complexes of this class relies on the availability of suitable methods for the introduction of cyclometalated C<sup>N</sup> ligands with different π-π\* transition energies. With the aim of finding alternative synthetic routes that both make use of easily accessible platinum precursors and allow a straightforward variation of the C<sup>N</sup> ligands, we set out to examine the potential of dichloro-bridged Pt(II) dimers [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(C<sup>N</sup>)<sub>2</sub>] as versatile starting materials for the synthesis of cyclometalated Pt(IV) complexes. Dimers of this kind with cyclometalated 2-arylpyridines have been known for a long time<sup>26,27</sup> and serve as excellent precursors of luminescent Pt(II) complexes.<sup>28–31</sup> Their synthesis typically involves the reaction of K<sub>2</sub>PtCl<sub>4</sub> with the 2-arylpyridine ligand (N<sup>ACH</sup>) in 1:1 molar ratio at 80 °C. If the reaction is performed in the presence of an excess of N<sup>ACH</sup>, mononuclear Pt(II) complexes *trans*-N,N-[PtCl(C<sup>N</sup>)(N<sup>ACH</sup>)] are obtained (Scheme 1),<sup>32–35</sup> and therefore the ligand:metal ratio must be carefully controlled. When 2,6-diarylpyridines are employed, dimers bearing the monocyclometalated ligand are obtained exclusively, even in the presence of a ligand excess.<sup>36</sup>

Previous works have examined bridge-cleavage reactions of [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(C<sup>N</sup>)<sub>2</sub>] dimers with pyridine ligands (L).<sup>26,37,38</sup> The monomeric complexes *cis*-N,N-[PtCl(C<sup>N</sup>)(L)] are formed first, as a result of the preferential cleavage of the Pt–Cl bond *trans* to the metalated aryl because of the strong kinetic *trans* effect of this carbon-donor moiety. Subsequent isomerization to the thermodynamically more stable *trans*-N,N-[PtCl(C<sup>N</sup>)(L)] complexes may take place in the presence of an excess of L through an associative mechanism if this ligand lacks bulky substituents; otherwise, the kinetic *cis*-N,N isomers were reported to be stable at room temperature (Scheme 1).<sup>26</sup> Two of these works employed 2-arylpyridines as the L ligand, showing that the *trans*-N,N isomer is obtained exclusively at high temperatures,<sup>26,37</sup> whereas a mixture of the *cis*- and *trans*-N,N isomers was observed in one case by performing the reaction at room temperature;<sup>38</sup> however, to the best of our knowledge, *cis*-N,N complexes bearing N-coordinated 2-arylpyridines have never been isolated.



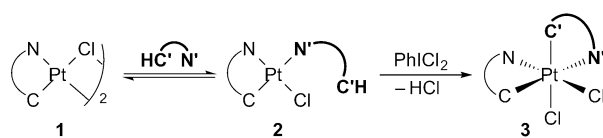
**Scheme 1.** HC<sup>N</sup> = 2-arylpyridine. L = (substituted) pyridine.

In the present work, we show that  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{C}^{\wedge}\text{N})_2]$  dimers, where C<sup>^N</sup> represents a monocyclusmetalated 2,6-diaryl- or 2-arylpyridine, can be employed to selectively synthesize Pt(IV) complexes of the type  $[\text{PtCl}_2(\text{C}^{\wedge}\text{N})(\text{C}'^{\wedge}\text{N}')]_2$ , bearing two different or equal cyclometalated ligands in an unsymmetrical arrangement, via bridge-cleavage reactions with different 2-arylpyridines (N'<sup>^C</sup>H) at room temperature and subsequent oxidation. The isolation and characterization of intermediate *cis-N,N*- $[\text{PtCl}(\text{C}^{\wedge}\text{N})(\text{N}'^{\wedge}\text{C}'\text{H})]$  complexes is reported for the first time and chloride substitution reactions on  $[\text{PtCl}_2(\text{C}^{\wedge}\text{N})(\text{C}'^{\wedge}\text{N}')]_2$  complexes are evaluated. A photophysical and computational study on a selected set of  $[\text{PtCl}_2(\text{C}^{\wedge}\text{N})(\text{C}'^{\wedge}\text{N}')]_2$  complexes is also presented, which provides a unique demonstration of the variability of the MLCT contribution to the essentially <sup>3</sup>LC emitting state of cyclometalated Pt(IV) complexes and its effects on their luminescence.

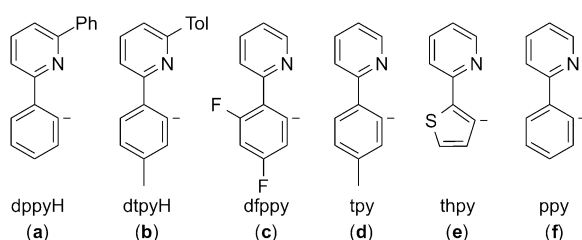
## Results and discussion

### Synthesis and characterization

The treatment of suspensions of dichloro-bridged dimers  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{C}^{\wedge}\text{N})_2]$  (**1**) in  $\text{CH}_2\text{Cl}_2$  with a 2-arylpyridine (N'<sup>^C</sup>H; 1–3 equiv per Pt) led to yellow or orange solutions containing monomeric Pt(II) species **2** that result from bridge-cleavage reactions (see Scheme 2 for the employed ligands and compound numbering). Isolation of complexes **2** was successful in some cases (**2af**, **2cd**, **2dd** and **2ed**), which allowed their unequivocal identification as *cis-N,N*- $[\text{PtCl}(\text{C}^{\wedge}\text{N})(\text{N}'^{\wedge}\text{C}'\text{H})]$  through X ray diffraction studies and/or NMR (see below). Although a previous study reported that the reaction of  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{tpy})_2]$  with tpyH gave a mixture of *cis*- and *trans-N,N*- $[\text{PtCl}(\text{tpy})(\text{tpyH})]$  isomers,<sup>38</sup> our results demonstrate that the *cis-N,N* isomer forms exclusively in all the studied cases.<sup>39</sup> Several experimental facts indicate that complexes **2** are in equilibrium with the parent dimers **1** and free N'<sup>^C</sup>H in solution, which appears to be more or less shifted toward the products depending on the properties of the C<sup>^N</sup> ligand. Thus, in all cases, the precursor **1** slowly precipitated from solutions of **2** in the absence of added N'<sup>^C</sup>H. For this reason, precipitation of pure samples or single-crystal formation of complexes **2af** and **2ed** from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  were only possible in the presence of an excess of the corresponding N'<sup>^C</sup>H ligand. The <sup>1</sup>H NMR spectrum of pure **2af** in  $\text{CD}_2\text{Cl}_2$  in the absence of ppyH showed very broad signals that indicate the existence of a mixture or a dynamic process (Fig. S1). The attempts to isolate complex **2bd** resulted in the precipitation of **1b**. Complexes **2cd**, **2dd** and **2ed** proved more stable than **2af** or **2bd** and their <sup>1</sup>H NMR spectra showed well-defined resonances, although small amounts of free tpyH were present too. Thus, it is clear that the formation of complexes **2** is more difficult from precursors **1a** or **1b**, which bear a monocyclusmetalated 2,6-diarylpyridine ligand that places the non-metalated aryl group in the vicinity of the coordination position of the incoming N'<sup>^C</sup>H ligand.



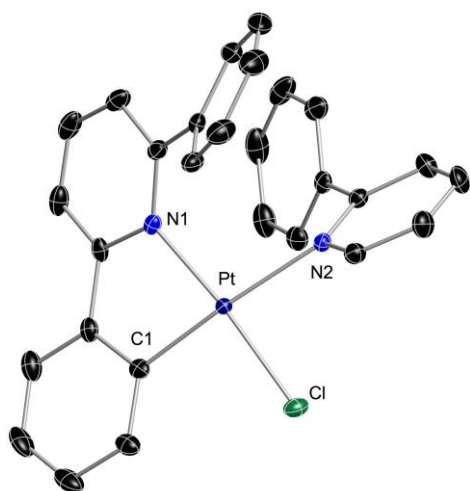
	$\overset{\curvearrowright}{\text{C}} \text{ N}$		$\overset{\curvearrowright}{\text{C}} \text{ N}$	$\overset{\curvearrowright}{\text{C}} \text{ N}'$
<b>1a</b>	dppyH	<b>2af</b>	<b>3af</b> dppyH	ppy
<b>1b</b>	dtpyH		<b>3ad</b> dppyH	tpy
<b>1c</b>	dfppy		<b>3bd</b> dtpyH	tpy
<b>1d</b>	tpy	<b>2cd</b>	<b>3cd</b> dfppy	tpy
<b>1e</b>	thpy		<b>3ce</b> dfppy	thpy
		<b>2dd</b>	<b>3dd</b> tpy	tpy
			<b>3de</b> tpy	thpy
		<b>2ed</b>	<b>3ed</b> thpy	tpy



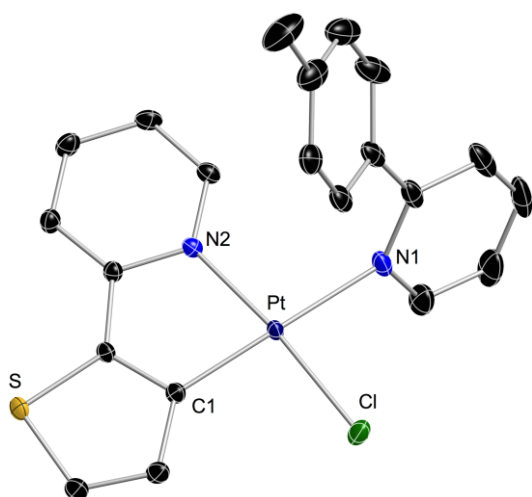
**Scheme 2.** Synthetic route to unsymmetrical bis-cyclometalated complexes **3**.

The  $^1\text{H}$  NMR spectra of complexes **2cd**, **2dd** and **2ed** are consistent with a *cis-N,N* configuration. A low-field shifted resonance at around 9.10 ppm arises from the aromatic proton ortho to the nitrogen of the coordinated tpyH ligand, while the resonance of the analogous proton in the cyclometalated C<sup>^</sup>N ligand is significantly high-field shifted, appearing together with the rest of aromatic signals, because it is directed toward the shielding region of the pyridine ring of the coordinated tpyH ligand. The NMR data also proved the absence of the *trans-N,N* isomers, which would give rise to a strongly shielded aromatic signal with platinum satellites at around 6 ppm corresponding to the proton ortho to the metalated carbon of the C<sup>^</sup>N ligand, which is directed toward the pyridine group of the tpyH ligand in these isomers.<sup>32</sup> The crystal structures of **2af** (Fig. 1) and **2ed** (Fig. 2) provided further confirmation of their *cis-N,N* configuration. In complex **2af**, the steric repulsion between the nonmetalated phenyl group of the dppyH ligand and the pyridine moiety of the ppyH ligand causes an appreciable deviation from the coplanarity between the three aromatic rings of the dppyH ligand and also determines the orientation of the coordinated pyridine ring of the ppyH ligand, which forms an angle of 55.8° with the Pt coordination mean plane. A similar twisted conformation of the dppyH ligand has been found for *cis*-[Pt(dppyH)<sub>2</sub>]<sup>40</sup> and [Pt(dppyH)(dmbpy)]<sup>+</sup> (dmbpy = 5,5'-dimethyl-2,2'-bipyridine).<sup>41</sup> In contrast, in **2ed** the thpy ligand and the coordination plane are practically coplanar (mean deviation from plane: 0.040 Å) and the pyridine group of the tpyH ligand forms an angle of 77° with the coordination plane. Treatment of CH<sub>2</sub>Cl<sub>2</sub> solutions of in situ generated complexes **2** with one equivalent of PhICl<sub>2</sub> led to the oxidation to Pt(IV) and the electrophilic metalation of the pendant aryl group of the coordinated N<sup>^</sup>C<sup>^</sup>H ligand to give unsymmetrical bis-cyclometalated complexes of the type [PtCl<sub>2</sub>(C<sup>^</sup>N)(C<sup>^</sup>N')] (**3**; Scheme 2), which could be isolated in moderate to good yields. Similar oxidation reactions have been previously employed for the synthesis of different types of bis-cyclometalated Pt(IV) complexes.<sup>15,17–19,42,43</sup> The formation of complexes **3** entails the liberation of one equivalent of HCl, which is trapped by the excess of N<sup>^</sup>C<sup>^</sup>H ligand present in the reaction mixture to give the

corresponding 2-arylpyridinium salt that can be removed by washing the crude solids with methanol. The main distinctive feature found in the  $^1\text{H}$  NMR spectra of complexes **3** is a resonance in the range 6.06–6.28 ppm flanked by platinum satellites, corresponding to the proton ortho to the metalated carbon of the C<sup>^N</sup> ligand, which is considerably shielded by the ring current of the aryl ring of the C<sup>^N</sup> ligand, indicating that the two metalated carbon atoms are mutually cis in all cases. The NMR data also ruled out ligand scrambling at room temperature.

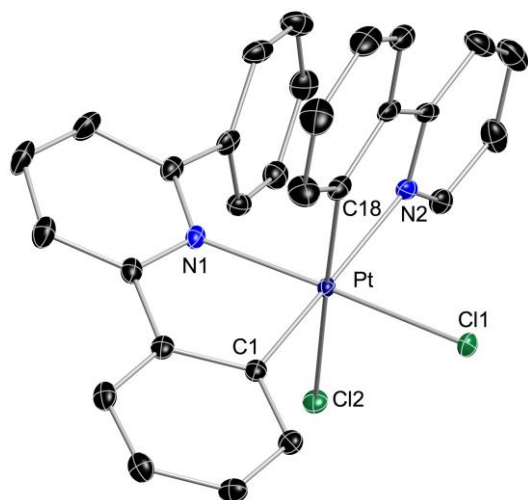


**Fig. 1.** Structure of **2af** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Pt–C1, 1.982(2); Pt–N1, 2.0447(19); Pt–N2, 2.159(2); Pt–Cl, 2.3004(6); C1–Pt–N1, 80.87(9); C1–Pt–Cl, 93.25(7); N1–Pt–N2, 100.72(8); N2–Pt–Cl, 84.88(6).

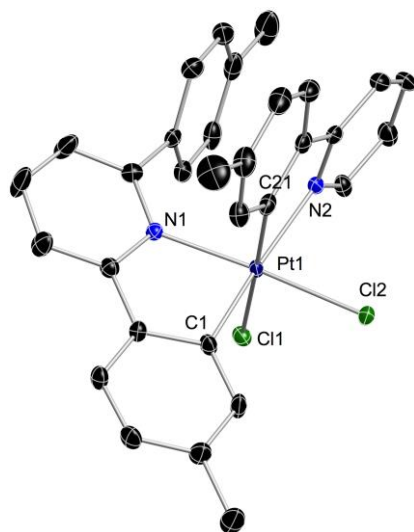


**Fig. 2.** Structure of one of the two independent molecules of **2ed** in the asymmetric unit (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Pt–C1, 1.975(2); Pt–N1, 2.1538(19); Pt–N2, 2.0321(18); Pt–Cl, 2.3041(6); C1–Pt–N2, 80.81(8); C1–Pt–Cl, 93.48(6); N1–Pt–N2, 97.51(7); N1–Pt–Cl, 88.15(6).

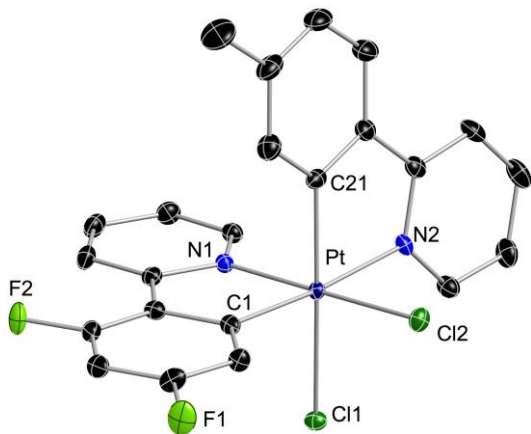
The crystal structures of **3af** (Fig. 3), **3bd** (Fig. 4) and **3cd** (Fig. 5) are consistent with the NMR data and also confirm that these derivatives retain the *cis-N,N* configuration of their precursors. The nonmetalated aryl ring of the dppyH or dtpyH ligand in complexes **3af** or **3bd** is rotated by about 67° with respect to the pyridine ring of the same ligand to minimize steric repulsions with the pyridine ring of the C'^N' ligand; still, these repulsions lead to some deviation from planarity in the cyclometalated portion of these ligands and longer Pt–N bond distances trans to Cl [**3af**, 2.0731(16) Å; **3bd**, 2.079(2) Å] as compared to the corresponding distance in **3cd** [2.0190(18) Å]. In the three cases, the Pt–C bond from the C'^N' ligand (trans to N) is appreciably shorter than the one from the C'^N' ligand (trans to Cl), suggesting that in these complexes the Cl ligand exerts a higher trans influence compared to the pyridine moiety of the C'^N' ligand.



**Fig. 3.** Structure of complex **3af** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Pt–C1, 2.006(2); Pt–Cl2, 2.4410(5); Pt–C18, 2.0179(19); Pt–N1, 2.0731(16); Pt–N2, 2.1402(17); Pt–Cl1, 2.3133(5); C1–Pt–N1, 81.39(7); C18–Pt–N2, 79.91(7); N1–Pt–N2, 100.15(6); Cl1–Pt–Cl2, 90.923(17).



**Fig. 4.** Structure of complex **3bd** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Pt–C1, 2.012(3); Pt–C21, 2.024(3); Pt–N1, 2.079(2); Pt–N2, 2.160(2); Pt–Cl2, 2.3166(6); Pt–Cl1, 2.4368(6); C1–Pt–N1, 80.85(9); C21–Pt–N2, 79.97(10); N1–Pt–N2, 103.09(8); Cl2–Pt–Cl1, 91.35(2).



**Fig. 5.** Structure of complex **3cd** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Pt–C1, 2.005(2); Pt–C21, 2.014(2); Pt–N1, 2.0190(18); Pt–N2, 2.1168(19); Pt–Cl2, 2.3142(5); Pt–Cl1, 2.4522(5); C1–Pt–N1, 81.06(9); C21–Pt–N2, 80.49(9); N1–Pt–N2, 96.48(7); Cl2–Pt–Cl1, 93.511(19).

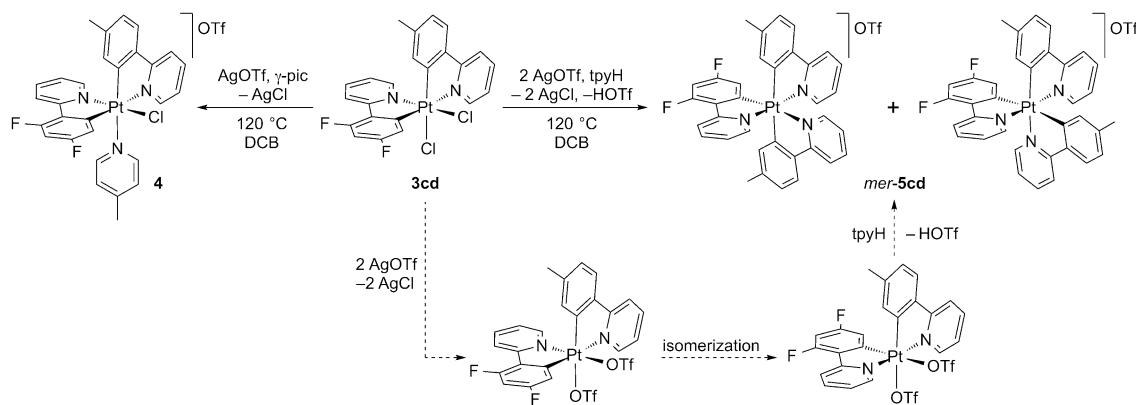
### Chloride substitution and C–C coupling reactions

Chloride substitution reactions in complexes **3** were investigated to evaluate their suitability as precursors of *fac* isomers of tris-cyclometalated Pt(IV) complexes, *fac*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup>. The only known route to this class of complexes involves the abstraction of the chloride ligands from the C<sub>2</sub>-symmetrical isomers of complexes [PtCl<sub>2</sub>(C<sup>^</sup>N)<sub>2</sub>] with 2 equiv of AgOTf in the presence of a third 2-arylpyridine ligand at high temperatures in noncoordinating solvents, affording exclusively the meridional isomers, *mer*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup>, which must then be photoisomerized to the *fac* isomers by irradiating with UV light.<sup>14,23,24</sup> Since the *mer*-to-*fac* photoisomerization step often results in low yields, direct synthetic routes to the *fac*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup> complexes are desirable. We hypothesized that the chloride ligand trans to the metalated carbon of the C<sup>^</sup>N' ligand would be abstracted first upon reaction with AgOTf, allowing the coordination of a third 2-arylpyridine ligand to form an intermediate with a *fac*-N,N,N configuration that would finally give the desired tris-cyclometalated complex. Toward testing this hypothesis, we first carried out the reaction of complex **3cd** with one equiv of AgOTf in the presence of  $\gamma$ -picoline ( $\gamma$ -pic) at 120 °C in 1,2-dichlorobenzene, which gave [PtCl(dfppy)(tpy)( $\gamma$ -pic)]OTf (**4**) in 65% yield (Scheme 3). The crystal structure of this complex (Fig. 6) showed that the coordinated nitrogen atoms are in a *fac* arrangement, demonstrating that the chloride trans to a metalated carbon in **3cd** was selectively substituted.

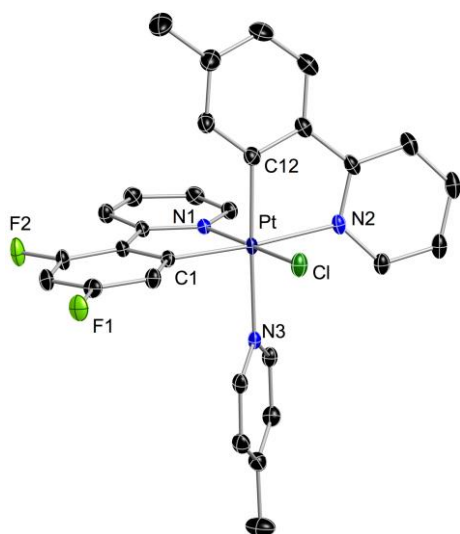
We then attempted the synthesis of tris-cyclometalated complexes from a subset of complexes **3** by abstracting the two chloride ligands in the presence of tpyH. Contrary to our expectations, the reaction of **3cd** with two equiv of AgOTf and an excess tpyH in 1,2-dichlorobenzene at 120 °C for 72 h gave a mixture of tris-cyclometalated complexes with a *mer* configuration, *mer*-[Pt(dfppy)(tpy)<sub>2</sub>]OTf (*mer*-**5cd**). The <sup>1</sup>H NMR spectrum of *mer*-**5cd** shows



two sets of aromatic resonances corresponding to two different species in a 1:0.7 ratio (Fig. S14 and S15), each one containing three inequivalent cyclometalated ligands, that we assign to two of the four possible isomers with a *mer* configuration (Scheme 3). Support for this assignment was obtained by irradiating a solution of this mixture in CD<sub>3</sub>CN in a quartz NMR tube with UV light, whereupon a single set of resonances gradually arose, also corresponding to three inequivalent ligands, which are attributable to the *fac* isomer (Fig. S15). The selective formation of two *mer* isomers in this reaction suggests that the intermediate species resulting from the abstraction of the chloride ligands, which must contain coordinated triflate anions, is unstable and isomerizes to a *trans-N,N* configuration under the reaction conditions (Scheme 3). We note that the C<sub>2</sub>-symmetrical complex [Pt(OTf)<sub>2</sub>(ppy)<sub>2</sub>] is stable in noncoordinating solvents.<sup>16</sup> The isomerization process must be faster than the coordination of the tpyH ligand through the N atom, which is probably hindered due to the presence of the *p*-tolyl substituent. Analogously, the reaction of **3dd** with two equiv of AgOTf and an excess tpyH in 1,2-dichlorobenzene at 120 °C for 72 h gave *mer*-[Pt(tpy)<sub>3</sub>]OTf (*mer*-**5dd**), which has been already reported<sup>14</sup> and was identified by its <sup>1</sup>H NMR data.



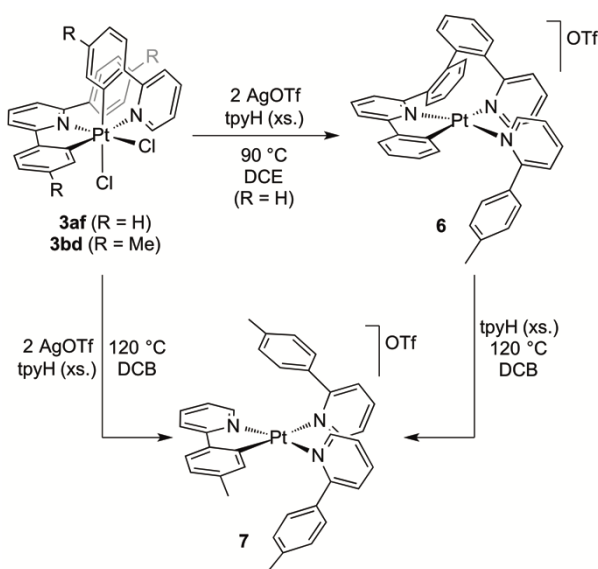
**Scheme 3.** Chloride substitution reactions of **3cd**. DCB = 1,2-Dichlorobenzene.



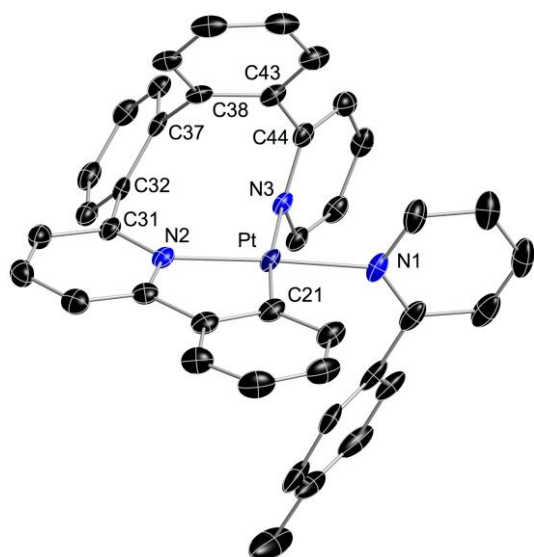
**Fig. 6.** Structure of complex **4**·Et<sub>2</sub>O (thermal ellipsoids at 50% probability). The triflate anion, hydrogen atoms and crystallization solvent are omitted. Selected bond distances (Å) and

angles (°): Pt–C1, 2.009(2); Pt–C12, 2.020(2); Pt–N1, 2.0365(17); Pt–N2, 2.1283(18); Pt–N3, 2.1718(18); Pt–Cl, 2.3081(6); C1–Pt–N1, 81.25(8); C12–Pt–N2, 80.46(8); N1–Pt–N2, 98.04(7); N3–Pt–Cl, 91.64(5).

Drastically different results were obtained when starting from complexes with dppyH or dtpyH ligands. The reaction of complex **3af** with 2 equiv of AgOTf and an excess tpyH (3–5 equiv) in 1,2-dichloroethane at 90 °C for 48 h afforded a mixture from which the yellow Pt(II) complex [Pt(C<sup>^</sup>N<sup>^</sup>N)(tpyH)]OTf (**6**) could be isolated (23% yield), containing a terdentate C<sup>^</sup>N<sup>^</sup>N ligand that results from a reductive C–C coupling between the metalated carbon of the ppy ligand and an ortho carbon from one of the phenyl groups of the dppyH ligand (Scheme 4). The identity of **6** was established by means of X ray diffraction studies (Fig. 7). The C<sup>^</sup>N<sup>^</sup>N ligand forms 5- and 9-membered chelate rings. The coordination environment around the metal deviates from the ideal square planar geometry because of the narrow bite angle of the C<sup>^</sup>N fragment of the C<sup>^</sup>N<sup>^</sup>N ligand [N2–Pt–C21, 81.59(12)°] and the strain caused by the 9-membered ring [N3–Pt–N2, 105.36(10)°]. As expected, the longest Pt–N bond distance corresponds to the nitrogen trans to the metalated carbon [Pt–N3, 2.155(3) Å]. The <sup>1</sup>H NMR spectrum of **6** confirms the presence of a coordinated tpyH ligand, which gives a resonance at 8.78 ppm due to the proton ortho to the coordinated nitrogen atom. It also corroborates that a phenyl group of the ppy fragment remains metalated, as evidenced by the resonance at 5.78 ppm with Pt satellites arising from the proton ortho to the metalated carbon, which is shielded because of its proximity to the ring current of the pyridine group of the tpyH ligand. The attempt to obtain a derivative analogous to **6** by reacting complex **3bd** with 2 equiv of AgOTf and an excess tpyH under the same conditions afforded a product mixture; although its <sup>1</sup>H NMR data suggested the presence of the C–C coupling product, all efforts to isolate it were unsuccessful.

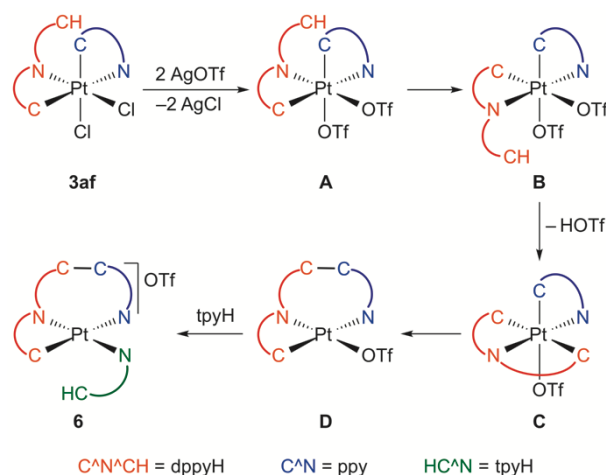


**Scheme 4.** Chloride substitution reactions of **3af** and **3bd**. DCE = 1,2-Dichloroethane. DCB = 1,2-Dichlorobenzene.



**Fig. 7.** Structure of complex **6**·0.5CH<sub>2</sub>Cl<sub>2</sub> (thermal ellipsoids at 50% probability). Hydrogen atoms and crystallization solvent are omitted. Selected bond distances (Å) and angles (°): Pt–N1, 2.042(3); Pt–N2, 2.062(3); Pt–N3, 2.155(3); Pt–C21, 1.983(3); N1–Pt–N3, 81.09(10); N3–Pt–N2, 105.36(10); N2–Pt–C21, 81.59(12); N1–Pt–C21, 91.21(12).

A possible reaction pathway for the formation of complex **6** is shown in Scheme 5. The abstraction of the chloride ligands in **3af** would lead to species **A**, containing labile triflate ligands, which would isomerize to give a species with a *trans*-*N,N* configuration (**B**). The metalation of the second phenyl ring of the dppyH ligand would then be possible, giving intermediate **C**. At this point, the reductive coupling of two mutually cis metalated carbon atoms would take place, resulting in the formation of the nine-membered ring (**D**). Finally, the substitution of the triflate ligand in **D** for tpyH would give the cationic complex **6**. This process is closely related to the reductive C–C couplings involving a dicyclopalladated 2,6-diarylpyridine ligand and a cyclometalated tribenzylphosphine ligand on the coordination sphere of Pt(IV), which have been recently reported by Rourke et al.<sup>44</sup>



**Scheme 5.** Proposed reaction pathway for the formation of complex **6**.

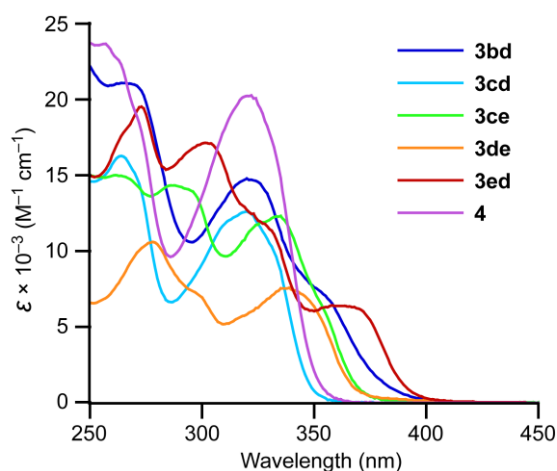
When a higher temperature was employed (120 °C in 1,2-dichlorobenzene for 48 h), the reactions of **3af** or **3bd** with AgOTf (2 equiv) and tpyH (5 equiv) gave [Pt(tpy)(tpyH)<sub>2</sub>]OTf (**7**), resulting from a reduction to Pt(II) and the replacement of all the ligands present in the Pt(IV) precursor by tpy or tpyH ligands (Scheme 4). Complex **7** could also be obtained by heating a mixture of **6** and tpyH (5 equiv) in 1,2-dichlorobenzene at 120 °C for 48 h, suggesting that its formation involves a transcyclometalation step in which the C<sup>^</sup>N<sup>^</sup>N ligand is replaced by tpy. A complex analogous to **7** containing 1-phenylisoquinoline ligands [Pt(piq)(piqH)<sub>2</sub>]OTf has been previously reported to result from the reaction of [PtCl<sub>2</sub>(piq)<sub>2</sub>] (C<sub>2</sub>-symmetrical isomer) with 2 equiv of AgOTf in the presence of an excess of piqH.<sup>23</sup>

### Photophysical study

The Pt(IV) complexes **3bd**, **3cd**, **3ce**, **3de**, **3ed** and **4** were selected for a photophysical study. Their electronic absorption data in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K are compiled in Table 1 and the spectra are shown in Fig. 8. The lowest-energy absorption bands in the range 300-400 nm apparently result from the overlap of ligand-centred (<sup>1</sup>LC) absorptions from the individual C<sup>^</sup>N and C<sup>^</sup>N' ligands, as has been observed for other Pt(IV) complexes containing different cyclometalated 2-arylpyridines.<sup>23</sup> Thus, complexes **3bd**, **3cd**, **3ed** and **4**, bearing tpy as the C<sup>^</sup>N' ligand, give rise to a common absorption feature at around 320 nm. Similarly, the lowest-energy shoulder at around 350 nm in the spectra of complexes **3ce** and **3de** is attributable to the cyclometalated thpy, which is the C<sup>^</sup>N' ligand in these derivatives and has the lowest π-π\* transition energy. Notably, the thpy absorption has a lower energy in complex **3ed**, where it can be distinguished as an individual band (359-371 nm), revealing that the same ligand gives a lower energy absorption when it occupies the C<sup>^</sup>N position. The long tails extending to ca. 450 nm that can be most clearly observed in the spectra of derivatives **3bd**, **3de** and **3ed** are typical of LMCT and/or LLCT absorptions, as observed for other bis-cyclometalated Pt(IV) complexes with halide ligands.<sup>16</sup>

**Table 1.** Electronic absorption data for the studied complexes in CH<sub>2</sub>Cl<sub>2</sub> solution (ca. 5 × 10<sup>-5</sup> M) at 298 K.

Complex	$\lambda_{max}/nm$ ( $\epsilon \times 10^{-2}/M^{-1} cm^{-1}$ )
<b>3bd</b>	264 (211), 320 (148), 353 (sh, 72)
<b>3cd</b>	264 (163), 309 (sh, 117), 320 (126), 332 (sh, 100)
<b>3ce</b>	262 (151), 286 (144), 296 (138), 327 (119), 335 (123), 354 (sh, 62)
<b>3de</b>	267 (196), 297 (73), 338 (75), 347 (sh, 69)
<b>3ed</b>	272 (195), 303 (172), 328 (sh, 117), 359 (65)
<b>4</b>	257 (237), 320 (202)



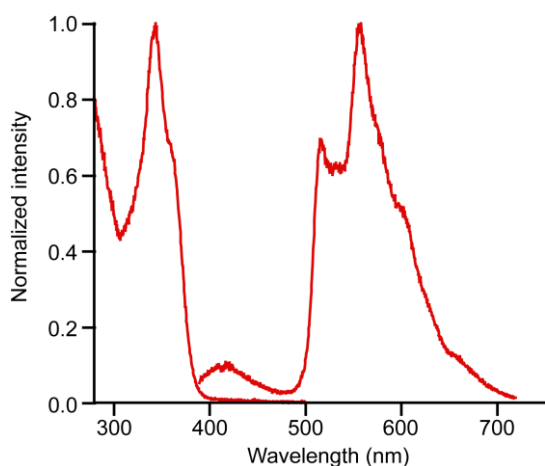
**Fig. 8.** Electronic absorption spectra of complexes **3bd**, **3cd**, **3ce**, **3de**, **3ed** and **4** in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K.

The luminescence of the selected subset of complexes was examined in deaerated CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K and in butyronitrile (PrCN) frozen glasses at 77 K. The emission data are summarized in Table 2 and the emission spectra are plotted in Fig. 9 and 10. Complexes **3bd**, **3ce** and **3de** showed no detectable emissions in fluid CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K, in line with the previously studied unsymmetrical isomers of complexes [PtX<sub>2</sub>(ppy)<sub>2</sub>] (X = halide or carboxylate), whose emissions are totally quenched at room temperature due to the thermal population of dissociative or distorted excited states of LMCT character.<sup>16</sup> Complexes **3cd**, **3ed** and **4** showed a weak but measurable luminescence in these conditions, but only in the case of **3ed** was the excitation spectrum compatible with the absorption profile (Fig. 9). Irradiation of diluted solutions of **3cd** and **4** in CH<sub>2</sub>Cl<sub>2</sub> with UV light (310 nm) led to substantial changes in their absorption spectra, and thus their emissions in this medium could arise from photodecomposition products. In contrast, CH<sub>2</sub>Cl<sub>2</sub> solutions of complex **3ed** proved photostable at 298 K. Its emission spectrum shows a vibrationally structured band (Fig. 9), with a large Stokes shift and a lifetime of 14.3 μs, consistent with a triplet ligand-centred (<sup>3</sup>LC) emitting excited state. This emission is very similar in energy and shape to those of [PtMe(Cl)(thpy)<sub>2</sub>]<sup>15</sup> or *mer*-[Pt(C<sup>^</sup>N)<sub>2</sub>(thpy)]<sup>+</sup> (C<sup>^</sup>N = dfppy, ppy),<sup>23</sup> meaning that the chromophoric ligand is the thpy.

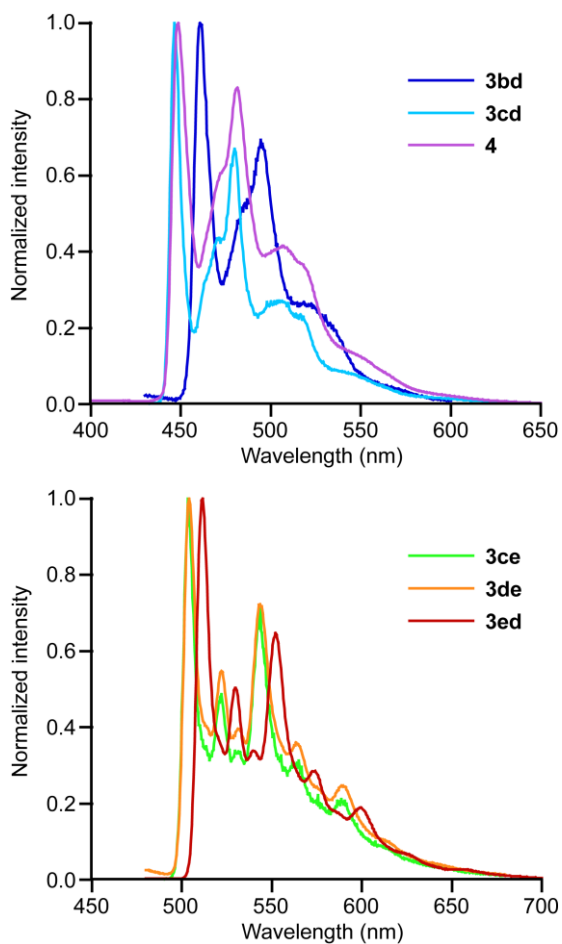
**Table 2.** Emission data of the studied complexes.

Complex	Medium (T/K)	$\lambda_{em}^a/nm$	$\tau^b/\mu s$
<b>3bd</b>	PrCN (77)	<i>460</i> , 494, 523	272
<b>3cd</b>	PrCN (77)	447, <i>480</i> , 506, 518, 543	662
<b>3ce</b>	PrCN (77)	503, 521, 543, 564, 589	497
<b>3de</b>	PrCN (77)	505, 523, 543, 564, 589	496
<b>3ed</b>	CH <sub>2</sub> Cl <sub>2</sub> (298)	518, <i>558<sup>c</sup></i>	14.3
	PrCN (77)	512, 530, 552, 573, 600	269
<b>4</b>	PrCN (77)	447, 480, 508, 518, 543	906

<sup>a</sup> The most intense peak is italicized. <sup>b</sup> Emission lifetime.



**Fig. 9.** Excitation (left) and emission (right) spectra of complex **3ed** in  $\text{CH}_2\text{Cl}_2$  solution at 298 K.



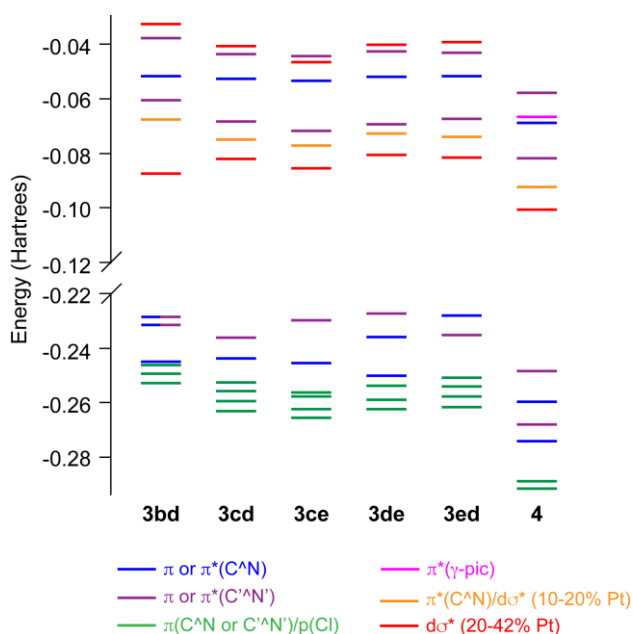
**Fig. 10.** Emission spectra of the studied complexes in PrCN frozen glasses at 77 K.

All of the studied complexes showed sharply structured emissions in PrCN glasses at 77 K (Fig. 10), with lifetimes in the range 269-906  $\mu\text{s}$ , which are typical of  $^3\text{LC}$  emissions from cyclometalated Pt(IV) complexes.<sup>14,23,24</sup> The vibrational structures and emission energies indicate that the observed luminescence arises from the cyclometalated ligand with the lowest

$\pi$ - $\pi^*$  transition energy, namely dtpyH (**3bd**), tpy (**3cd**, **4**) or thpy (**3ce**, **3de**, **3ed**). The emission energy of **3ed** is lower than that of its isomeric complex **3de**, meaning that the essentially LC transition within the chromophoric thpy ligand has a lower energy when it occupies the C<sup>^</sup>N position (C trans to N') than when it is in the C'<sup>^</sup>N' position (C' trans to Cl). This is consistent with the lower energy observed for the thpy absorption band observed for **3ed** with respect to **3de** (see above). It is also noteworthy that complexes that emit from the ligand in the C<sup>^</sup>N position (**3bd** and **3ed**) display significantly shorter emission lifetimes compared to the rest of studied complexes, which could be associated with a higher effectiveness of the spin-orbit coupling induced by the metal, resulting in faster radiative decays.<sup>1,10,45,46</sup>

### Computational study

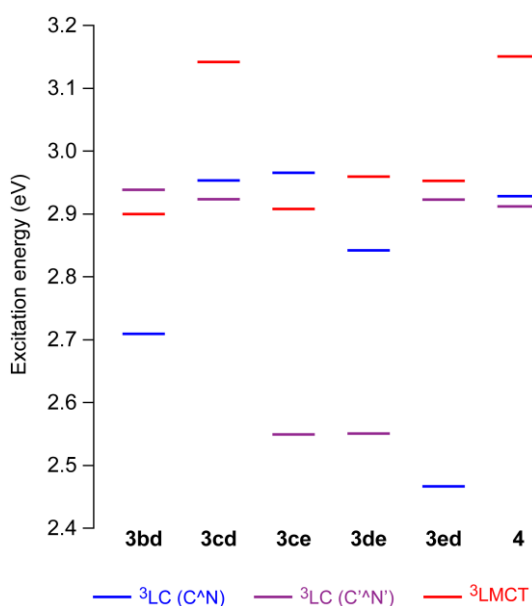
For a better understanding of their photophysical properties, DFT and TD-DFT calculations have been performed for complexes **3bd**, **3cd**, **3ce**, **3de**, **3ed** and **4** at the B3LYP/(6-31G\*\*+LANL2DZ) level considering solvent effects (CH<sub>2</sub>Cl<sub>2</sub>). Fig. 11 shows a diagram comparing frontier orbital energies and a simplified, color-coded representation of their composition. Detailed compositions and isodensity surfaces of frontier orbitals are given in the ESI. The highest occupied molecular orbital (HOMO) and the HOMO-1 are essentially  $\pi$  orbitals of the C<sup>^</sup>N or C'<sup>^</sup>N' ligands with little metal orbital involvement (1–4%). The lowest unoccupied molecular orbital (LUMO) is a  $d\sigma^*$  orbital mainly distributed along the N–Pt–Cl axis, while the LUMO+1 is a  $\pi^*$  orbital of the C<sup>^</sup>N ligand with significant  $d\sigma^*$  character along the mentioned axis. Essentially  $\pi^*$  orbitals of the C<sup>^</sup>N and C'<sup>^</sup>N' ligands lie at higher energies. Among complexes **3**, the largest HOMO-LUMO energy gap is found for **3cd**, mainly because its tpy-based HOMO has a lower energy compared to the dtpyH- or thpy-based HOMOs of the other complexes. The dtpyH complex **3bd** presents the smallest HOMO-LUMO gap, mainly because of its low LUMO energy, which can reasonably be connected to the weaker  $\sigma$ -donation from the pyridine moiety of the dtpyH ligand as a consequence of the longer Pt–N(dtpyH) bond distance. Frontier orbital energies in complex **4** are lower than in complexes **3** because of its cationic nature, but its HOMO-LUMO gap is similar to that of its precursor **3cd**.



**Fig. 11.** Orbital energy diagrams from DFT calculations.

Excitation energies at the ground-state geometries were calculated by TDDFT in CH<sub>2</sub>Cl<sub>2</sub> solution. The data for selected singlet and triplet excitations are given in the ESI. The lowest-energy singlet excitations have low oscillator strengths and correspond to primarily LMCT transitions from the HOMO or HOMO-1 to the LUMO, and are consistent with the long tails observed in the absorption spectra. The excitations with the highest oscillator strengths correspond to <sup>1</sup>LC ( $\pi$ - $\pi^*$ ) transitions within the C<sup>^N</sup> or C<sup>^N'</sup> ligands with some LMCT character. Consistent with the experimental observations, the lowest <sup>1</sup>LC excitation in complexes **3ce**, **3de** and **3ed** involves the thpy ligand and has a lower energy for **3ed**, where the thpy ligand occupies the C<sup>^N</sup> position.

A diagram showing the lowest vertical triplet excitation energies at the ground-state geometries and their main character is shown in Fig. 12. The T<sub>1</sub> excitation in complexes **3bd** and **3ed** corresponds to a HOMO-LUMO+1 transition, and therefore can be described as <sup>3</sup>LC involving the C<sup>^N</sup> ligand (dtpyH or thpy, respectively), with some LMCT character. In the rest of complexes, the T<sub>1</sub> arises from a HOMO-LUMO+2 excitation, which is a  $\pi$ - $\pi^*$  transition within the C<sup>^N'</sup> ligand [tpy (**3cd**, **4**) or thpy (**3ce**, **3de**)], and can be described as almost purely <sup>3</sup>LC. Thus, in all cases the lowest triplet excitation involves the cyclometalated ligand with the lowest  $\pi$ - $\pi^*$  transition energy, which agrees with the experimental emission data. The lower T<sub>1</sub> excitation energy predicted for complex **3ed** relative to the other thpy-based emitters is also consistent with the experimental observations. All the studied complexes present low-lying <sup>3</sup>LMCT excited states, whose energies approximately correlate with the HOMO-LUMO energy gaps, and therefore are lower for the complexes bearing the dtpyH (**3bd**) or thpy (**3ce**, **3de**, **3ed**) ligands. The energy differences between the lowest <sup>3</sup>LMCT state and the T<sub>1</sub> state range from 0.19 (**3bd**) to 0.49 (**3ed**) eV. These differences are smaller compared with those found for other cyclometalated Pt(IV) complexes that are moderately emissive in fluid solution, e.g. [PtCl<sub>2</sub>(ppy)<sub>2</sub>] (C<sub>2</sub>-symmetrical isomer, 0.60 eV)<sup>16</sup> or *mer*-[Pt(ppy)<sub>2</sub>(thpy)]<sup>+</sup> (1.15 eV),<sup>23</sup> meaning that thermal population of the LMCT state from the emitting state should provide an effective nonradiative deactivation mechanism, resulting in largely or totally quenched emissions at room temperature.



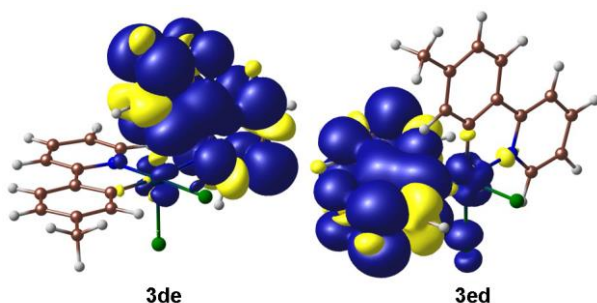
**Fig. 12.** Lowest triplet excitation energies from TDDFT calculations at the ground-state geometry.



The geometry of the lowest triplet excited state ( $T_1$ ) was optimized for **3cd**, **3ce**, **3de**, **3ed** and **4**. In the case of **3bd**, the  $T_1$  state could not be optimized because it collapsed to a dissociative LMCT state. The calculated electronic energies relative to the ground state (adiabatic energy differences, Table 3) are in good agreement with the observed sequence of emission energies. The spin density distributions correspond to  $\pi$ - $\pi^*$  excitations mainly localized on the cyclometalated ligands (Fig. 13 and S37) with little metal orbital participation. Notably, there is an appreciably higher spin density on the metal in the  $T_1$  state of **3ed** with respect to the other complexes, which can be visually appreciated by comparing the spin density distributions for the  $T_1$  state of the isomeric complexes **3de** and **3ed** (Fig. 13). Consistently, the calculated natural spin density on the Pt atom (Table 3) is appreciably higher for the  $T_1$  state of **3ed**, which implies a higher metal-orbital contribution to the excited state. This fact can be reasonably ascribed to a stronger  $\pi$ -donation from the aryl group of the chromophoric thpy ligand in **3ed**, where it occupies the C^N position (C trans to N') and has a shorter Pt–C bond distance, resulting in a higher energy of the involved  $d\pi$  orbital and hence it can be associated with a higher degree of MLCT admixture into the relaxed  $^3LC$  state, which is consistent with its lower energy relative to **3ce** and **3de**. In the other complexes, the chromophoric ligand occupies the C'^N' position (C' trans to Cl) and the corresponding Pt–C' distance is longer, resulting in a much lower spin density on the metal and hence a markedly decreased MLCT contribution. This implies also that complexes that emit from the C^N ligand (**3bd** and **3ed**) may exhibit shorter emission lifetimes due to an enhancement of the spin-orbit coupling effects induced by the metal, which are known to accelerate the radiative transition to the ground state.<sup>1,10,45,46</sup>

**Table 3.** Adiabatic energy differences between the  $T_1$  and  $S_0$  states and natural spin densities at the Pt atom in the optimized  $T_1$  state.

Complex	$\Delta E(T_1-S_0)/\text{eV}$	Spin density on Pt
<b>3cd</b>	2.81	0.0062
<b>3ce</b>	2.38	0.0082
<b>3de</b>	2.38	0.0094
<b>3ed</b>	2.32	0.0347
<b>4</b>	2.79	0.0017



**Fig. 13.** Spin density distributions ( $0.001 \text{ e bohr}^{-3}$ ) for the lowest triplet excited state of complexes **3de** and **3ed**.

On the basis of these computational results, the fact that **3ed** is the only complex of the studied series that emits in fluid solution at 298 K is a consequence of two favourable

factors: (1) it is the derivative with the largest energy difference between the emitting state and the lowest <sup>3</sup>LMCT state, and therefore its emission should be less effectively quenched, and (2) the chromophoric thpy ligand occupies the C<sup>^</sup>N position, having a higher metal orbital involvement in the emitting state, which implies a faster radiative transition to the ground state.

## Conclusions

Dichloro-bridged dimers [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(C<sup>^</sup>N)<sub>2</sub>], bearing a monocyclometalated 2,6-diaryl- or 2-arylpyridine ligand (C<sup>^</sup>N) undergo bridge-cleavage reactions upon reaction with different 2-arylpyridines (N<sup>'</sup>C<sup>'</sup>H) at room temperature to give exclusively complexes *cis*-N,N-[PtCl(C<sup>^</sup>N)(N<sup>'</sup>C<sup>'</sup>H)]; isolation and structural characterization of derivatives of this class have been achieved for the first time. Subsequent oxidation with PhICl<sub>2</sub> leads to the electrophilic metalation of the pendant aryl group of the N<sup>'</sup>C<sup>'</sup>H ligand to give Pt(IV) complexes [PtCl<sub>2</sub>(C<sup>^</sup>N)(C<sup>'</sup>N<sup>'</sup>)], bearing two different or equal cyclometalated ligands in an unsymmetrical arrangement.

Chloride-abstraction reactions on a subset of complexes [PtCl<sub>2</sub>(C<sup>^</sup>N)(C<sup>'</sup>N<sup>'</sup>)] using AgOTf at 120 °C have been investigated to evaluate their suitability for the synthesis of tris-cyclometalated Pt(IV) complexes. The selective substitution of the chloride ligand *trans* to C<sup>'</sup> can be achieved by using one equiv of AgOTf. However, when both chloride ligands are abstracted in the presence of a 2-arylpyridine, isomerization to intermediate complexes with a *trans*-N,N configuration occurs, resulting in the formation of *mer* isomers of tris-cyclometalated Pt(IV) complexes if C<sup>^</sup>N is a monoarylpyridine, or in a reductive C–C coupling reaction if C<sup>^</sup>N is a monocyclometalated 2,6-diarylpyridine.

Complexes of the type [PtCl<sub>2</sub>(C<sup>^</sup>N)(C<sup>'</sup>N<sup>'</sup>)] exhibit phosphorescence in frozen PrCN glasses arising from <sup>3</sup>LC states localized on the cyclometalated ligand with the lowest π-π\* transition energy, which can be either in the C<sup>^</sup>N (C *trans* to N<sup>'</sup>) or C<sup>'</sup>N<sup>'</sup> position (C<sup>'</sup> *trans* to Cl). The emissions are largely or totally quenched in fluid CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature because of the thermal population of low-lying, dissociative excited states of LMCT character. Interestingly, the complexes in which the chromophoric ligand occupies the C<sup>^</sup>N position exhibit shorter emission lifetimes and can have a lower emission energy with respect to those with the chromophoric ligand in the C<sup>'</sup>N<sup>'</sup> position. On the basis of the computational analysis, this effect can be ascribed to a higher MLCT admixture into the essentially <sup>3</sup>LC emitting state for the ligands in the C<sup>^</sup>N position, because of the shorter Pt–C bond distance *trans* to N<sup>'</sup> and a stronger π-donation from the aryl group, which increases the energy of the occupied dπ orbitals. Thus, the present results show that, although the metal orbital contribution to the emitting state in cyclometalated Pt(IV) complexes is small, it can be modulated by varying the ligand *trans* to the metalated carbon of the chromophoric ligand and can have an appreciable impact on their emission properties.

## Experimental Section

### General considerations, materials and instrumentation

Unless otherwise noted, preparations were carried out at room temperature under atmospheric conditions using synthesis grade solvents. The dichloro-bridged dimers **1a**<sup>36</sup> and

**1b**<sup>25</sup> and the  $\text{PhICl}_2$ <sup>47</sup> reagent were prepared following reported procedures. NMR spectra were recorded on Bruker Advance 300, 400 or 600 MHz spectrometers at 298 K. Chemical shifts ( $\delta$ ) were referenced to residual signals of non-deuterated solvent and are given in ppm downfield from tetramethylsilane. Elemental analyses were carried out with a LECO CHNS-932 microanalyzer. High-resolution electrospray ionization mass spectra (ESI-MS) were recorded on an Agilent 6220 Accurate-Mass time-of-flight (TOF) LC/MS. The irradiation of *mer-5cd* was carried out using a 36 W Philips UVB Narrowband lamp centred at 310 nm. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 750S spectrophotometer. Excitation and emission spectra were recorded on a Jobin Yvon Fluorolog 3-22 spectrofluorometer with a 450 W xenon lamp, double-grating monochromators, and a TBX-04 photomultiplier. Measurements were carried out in a right angle configuration using 10 mm quartz fluorescence cells (298 K) or 5 mm quartz NMR tubes (77 K). A liquid nitrogen Dewar with quartz windows was employed for the low-temperature measurements. Solutions of the samples were degassed by bubbling argon for 30 min. Lifetimes were measured using an IBH FluoroHub controller in MCS mode and the Fluorolog's FL-1040 phosphorimeter pulsed xenon lamp as excitation source; the estimated uncertainty is  $\pm 10\%$  or better.

**General procedure for the synthesis of  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{C}^{\wedge}\text{N})_2]$  ( $\text{C}^{\wedge}\text{N} = \text{dfppy}$  (**1c**), **tpy** (**1d**), **thpy** (**1e**)).** The following procedure is a modification of that reported for the  $\text{ppy}$ <sup>26</sup> and  $\text{tpy}$ <sup>38</sup> derivatives.  $\text{K}_2\text{PtCl}_4$  and the appropriate  $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$  ligand in 1:1 molar ratio were placed in a Carius tube under a  $\text{N}_2$  atmosphere and a previously degassed 3:1 (v/v) mixture of 2-ethoxyethanol and  $\text{H}_2\text{O}$  (50 mL) was added. The mixture was stirred at 80 °C for 24 h, whereupon a yellow suspension formed. After cooling to room temperature,  $\text{H}_2\text{O}$  (50 mL) was added to complete the precipitation. The solid was collected by filtration, washed with MeOH ( $2 \times 5$  mL),  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL) and  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and vacuum-dried to give **1**. All complexes **1** are insoluble in noncoordinating organic solvents.

**$[\text{Pt}_2(\mu\text{-Cl})_2(\text{dfppy})_2]$  (**1c**).** Yellow solid, obtained from  $\text{K}_2\text{PtCl}_4$  (1008 mg, 2.43 mmol) and  $\text{dfppyH}$  (370  $\mu\text{L}$ , 2.43 mmol). Yield: 694 mg, 68%. Elemental analysis calcd for  $\text{C}_{22}\text{H}_{12}\text{Cl}_2\text{F}_4\text{N}_2\text{Pt}_2$ : C, 31.40; H, 1.44; N, 3.33; found: C, 31.68; H, 1.35; N, 3.23.

**$[\text{Pt}_2(\mu\text{-Cl})_2(\text{tpy})_2]$  (**1d**).** Yellow solid, obtained from  $\text{K}_2\text{PtCl}_4$  (1643 mg, 3.96 mmol) and  $\text{tpyH}$  (677  $\mu\text{L}$ , 3.96 mmol). Yield: 905 mg, 57%. Elemental analysis calcd for  $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pt}_2$ : C, 36.15; H, 2.53; N, 3.51; found: C, 36.28; H, 2.40; N, 3.50.

**$[\text{Pt}_2(\mu\text{-Cl})_2(\text{thpy})_2]$  (**1e**).** Yellow solid, obtained from  $\text{K}_2\text{PtCl}_4$  (1000 mg, 2.41 mmol) and  $\text{thpyH}$  (420 mg, 2.53 mmol). Yield: 745 mg, 79%. Elemental analysis calcd for  $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{N}_2\text{Pt}_2\text{S}_2$ : C, 27.66; H, 1.55; N, 3.58; S, 8.20; found: C, 27.59; H, 1.45; N, 3.43; S, 8.44.

**General procedure for the synthesis of *cis-N,N*- $[\text{PtCl}(\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{C}^{\wedge}\text{H})]$  (**2**).** To a suspension of **1** (0.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added the  $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$  ligand (1-3 equiv per Pt) and the mixture was stirred until a clear solution was obtained (0.5-1 h). The mixture was concentrated under reduced pressure (1 mL) and  $\text{Et}_2\text{O}$  (15 mL) was added, whereupon a yellow solid precipitated, which was collected by filtration and vacuum dried to give **2**.

***cis-N,N*- $[\text{PtCl}(\text{dppyH})(\text{ppyH})]$  (**2af**).** Yellow solid, obtained from **1a** (80 mg, 0.09 mmol) and  $\text{ppyH}$  (80  $\mu\text{L}$ , 0.56 mmol). Yield: 97 mg, 88%. Elemental analysis calcd for  $\text{C}_{28}\text{H}_{21}\text{ClN}_2\text{Pt}$ : C, 54.59; H, 3.44; N, 4.55; found: C, 54.36; H, 3.57; N, 4.53. NMR data could not be obtained (see main text and Fig. S1).

**cis-N,N-[PtCl(dfppy)(tpyH)] (2cd).** Yellow solid, obtained from **1c** (60 mg, 0.07 mmol) and tpyH (40  $\mu$ L, 0.24 mmol). Yield: 47 mg, 56%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 9.09 (br d,  $J$  = 5.7 Hz, 1H, CH), 8.03–7.97 (m, 3H, CH), 7.93–7.86 (m, 1H, CH), 7.75 (td,  $J$  = 7.9, 1.7 Hz, 1H, CH), 7.71 (br d,  $J$  = 7.9 Hz, 1H, CH), 7.64–7.45 (m, 3H, CH), 7.18 (d,  $J$  = 7.8 Hz, 2H, CH), 6.81 (ddd,  $J$  = 7.4, 5.8, 1.5 Hz, 1H, CH), 6.56 (ddd,  $J$  = 12.6, 8.9, 2.5 Hz, 1H, CH), 2.27 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 164.4 (d,  $J_{\text{FC}}$  = 7 Hz, C), 162.6 (dd,  $J_{\text{FC}}$  = 255, 13 Hz, C), 161.3 (s, C), 160.0 (dd,  $J_{\text{FC}}$  = 258, 12 Hz, C), 153.0 (s, CH), 148.2 (s, CH), 143.0 (d,  $J_{\text{FC}}$  = 8 Hz, C), 140.3 (s, C), 139.2 (s, CH), 138.9 (s, CH), 136.5 (s, C), 130.0 (s, CH), 129.3 (s, CH), 127.7 (s, CH), 124.2 (s, CH), 122.8 (d,  $J_{\text{FC}}$  = 19 Hz, C), 122.6 (s, CH), 117.1 (d with satellites,  $J_{\text{FC}}$  = 19 Hz,  $J_{\text{PtC}} \sim 47$  Hz, CH), 99.6 (t,  $J_{\text{PtC}}$  = 27 Hz, CH), 21.6 ( $\text{CH}_3$ ); the resonance of one of the quaternary carbon atoms was not observed. Elemental analysis calcd for  $\text{C}_{23}\text{H}_{17}\text{ClF}_2\text{N}_2\text{Pt}$ : C, 46.83; H, 2.90; N, 4.75; found: C, 46.78; H, 2.84; N, 4.67.

**cis-N,N-[PtCl(tpy)(tpyH)] (2dd).** Yellow solid, obtained from **1d** (80 mg, 0.10 mmol) and tpyH (102  $\mu$ L, 0.60 mmol). Yield: 54 mg, 48%.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 9.11 (br d,  $J_{\text{HH}}$  = 5.5 Hz, 1H, CH), 8.04 (d,  $J_{\text{HH}}$  = 7.7 Hz, 2H, CH), 7.99 (td,  $J_{\text{HH}}$  = 7.8, 1.7 Hz, 1H, CH), 7.75 (s with satellites,  $J_{\text{PtH}}$  = 17 Hz, 1H, CH), 7.73–7.59 (m, 2H, CH), 7.53–7.45 (m, 3H, CH), 7.23 (d,  $J_{\text{HH}}$  = 7.9 Hz, 1H, CH), 7.19 (d,  $J_{\text{HH}}$  = 7.9 Hz, 2H, CH), 6.87 (d,  $J_{\text{HH}}$  = 7.8 Hz, 1H, CH), 6.75–6.70 (m, 1H, CH), 2.34 (s, 3H,  $\text{CH}_3$ ), 2.27 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 167.9 (C), 161.3 (C), 153.1 (CH), 148.0 (CH), 142.5 (C), 140.2 (C), 138.9 (C), 138.9 (CH), 138.1 (CH), 136.7 (C), 135.7 (CH), 130.1 (CH), 129.2 (CH), 127.5 (CH), 124.9 (CH), 124.0 (CH), 123.4 (CH), 122.0 (CH), 118.9 (CH), 22.1 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{Pt}$ : C, 50.75; H, 3.73; N, 4.93; found: C, 50.74; H, 3.75; N, 4.80.

**cis-N,N-[PtCl(thpy)(tpyH)] (2ed).** Orange solid, obtained from **1e** (150 mg, 0.19 mmol) and tpyH (90  $\mu$ L, 0.53 mmol). Yield: 173 mg, 80%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 9.10 (ddd with satellites,  $J_{\text{HH}}$  = 5.7, 1.7, 0.8 Hz,  $J_{\text{PtH}}$  = 18 Hz, 1H, CH), 8.04 (d with satellites,  $J_{\text{HH}}$  = 8.2 Hz,  $J_{\text{PtH}}$  = 8 Hz, 2H, CH), 7.98 (td,  $J_{\text{HH}}$  = 7.8, 1.7 Hz, 1H, CH), 7.69 (ddd,  $J_{\text{HH}}$  = 7.9, 1.4, 0.8 Hz, 1H, CH), 7.59 (td,  $J_{\text{HH}}$  = 7.8, 1.5 Hz, 1H, CH), 7.48 (ddd,  $J_{\text{HH}}$  = 7.2, 5.6, 1.5 Hz, 1H, CH), 7.42 (d with satellites,  $J_{\text{HH}}$  = 4.8 Hz,  $J_{\text{PtH}} \sim 6$  Hz, 1H, CH), 7.35 (ddd,  $J_{\text{HH}}$  = 5.9, 1.5, 0.8 Hz, 1H, CH), 7.32 (d,  $J_{\text{HH}}$  = 4.8 Hz, 1H, CH), 7.23–7.18 (m, 3H, CH), 6.60 (ddd,  $J_{\text{HH}}$  = 7.4, 5.9, 1.5 Hz, 1H, CH), 2.28 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 163.3 (C), 161.3 (C), 153.1 (CH), 148.3 (CH), 143.5 (C), 140.3 (C), 139.0 (CH), 138.9 (CH), 136.6 (C), 133.3 ( $J_{\text{PtC}}$  = 93 Hz, CH), 130.0 (CH), 129.3 (CH), 127.4 (CH), 124.2 ( $J_{\text{PtC}}$  = 19 Hz, CH), 120.0 ( $J_{\text{PtC}}$  = 36 Hz, CH), 117.9 ( $J_{\text{PtC}}$  = 42 Hz, CH), 21.2 ( $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{21}\text{H}_{17}\text{ClN}_2\text{PtS}$ : C, 45.04; H, 3.06; N, 5.00; S, 5.73; found: C, 45.13; H, 3.06; N, 4.85; S, 5.41.

**General procedure for the synthesis of complexes 3.** The following procedure was applied in all cases except **3ed**. To a suspension of the dimer **1** (0.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added the appropriate  $\text{N}^1\text{C}^1\text{H}$  ligand (1-3 equiv per Pt). After stirring for 0.5 - 1 h, a clear yellow solution was obtained (in the synthesis of **3ce**, this mixture remained a suspension after 18 h).  $\text{PhICl}_2$  (1 equiv per Pt) was then added, whereupon an immediate colour change to pale yellow was observed. The mixture was concentrated under reduced pressure (2 mL) and  $\text{Et}_2\text{O}$  (15 mL) was added to give a pale-yellow precipitate, which was collected by filtration, washed with MeOH (3  $\times$  4 mL) and vacuum-dried to give the corresponding complex **3** (complex **3ce** precipitated directly from the  $\text{CH}_2\text{Cl}_2$  solution as a white solid after the addition of  $\text{PhICl}_2$ ).

**[PtCl<sub>2</sub>(dppyH)(ppy)] (3af).** Pale yellow solid, obtained from **1a** (80 mg, 0.09 mmol), ppyH (80  $\mu$ L, 0.56 mmol) and  $\text{PhICl}_2$  (50 mg, 0.18 mmol). Yield: 101 mg, 86%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):

$\delta$  = 8.78 (ddd with satellites,  $J_{\text{HH}} = 5.5, 1.3, 1.1$  Hz,  $J_{\text{PTH}} = 9$  Hz, 1H, CH), 8.21–8.13 (m, 1H, CH), 8.00 (dd,  $J_{\text{HH}} = 8.2, 1.6$  Hz, 1H, CH), 7.83–7.78 (m, 2H, CH), 7.70–7.65 (m, 3H, CH), 7.60 (dd,  $J_{\text{HH}} = 7.7, 1.4$  Hz, 1H, CH), 7.43 (dtd,  $J_{\text{HH}} = 16.8, 7.3, 1.6$  Hz, 2 H, CH), 7.28 (tdd,  $J_{\text{HH}} = 7.6, 1.4, 0.6$  Hz, 1H, CH), 7.14–7.04 (m, 2H, CH), 7.02 (td,  $J_{\text{HH}} = 5.4, 3.5$  Hz, 1H, CH), 6.89 (ddd,  $J_{\text{HH}} = 7.9, 7.3, 1.5$  Hz, 1H, CH), 6.83 (dd with satellites,  $J_{\text{HH}} = 7.5, 1.6$  Hz,  $J_{\text{PTH}} = 12$  Hz, 1H, CH), 6.74–6.64 (m, 1H, CH), 6.35 (dddd,  $J_{\text{HH}} = 7.6, 2.0, 1.2, 0.6$  Hz, 1H, CH), 6.28 (dd with satellites,  $J_{\text{HH}} = 7.9, 1.1$  Hz,  $J_{\text{PTH}} = 36$  Hz, 1H, CH).  $^{13}\text{C}$  NMR data could not be obtained because of the very low solubility of this complex in common solvents. Elemental analysis calcd for  $\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pt}$ : C, 51.70; H, 3.10; N, 4.31; found: C, 51.57; H, 3.07; N, 4.54.

**[PtCl<sub>2</sub>(dppyH)(tpy)] (3ad).** Pale yellow solid, obtained from **1a** (80 mg, 0.09 mmol), tpyH (80  $\mu\text{L}$ , 0.47 mmol) and  $\text{PhICl}_2$  (50 mg, 0.18 mmol). Yield: 72 mg, 60%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.75 (br d,  $J_{\text{HH}} = 4.9$  Hz, 1H, CH), 8.16 (d with satellites,  $J_{\text{HH}} = 7.6$  Hz,  $J_{\text{PTH}} = 25$  Hz, 1H, CH), 8.01 (d,  $J_{\text{HH}} = 8.1$  Hz, 1H, CH), 7.83–7.77 (m, 2H, CH), 7.68–7.59 (m, 3H, CH), 7.49–7.38 (m, 3H, CH), 7.27 (t,  $J_{\text{HH}} = 7.6$  Hz, 1H, CH), 7.08 (td,  $J_{\text{HH}} = 7.6, 6.4$  Hz, 1H, CH), 7.00–6.95 (m, 1H, CH), 6.91 (d,  $J_{\text{HH}} = 7.9$  Hz, 1H, CH), 6.83 (d,  $J_{\text{HH}} = 7.4$  Hz, 1H, CH), 6.68 (t,  $J_{\text{HH}} = 7.6$  Hz, 1H, CH), 6.35 (d,  $J_{\text{HH}} = 7.4$  Hz, 1H, CH), 6.06 (s with satellites,  $J_{\text{PTH}} = 37$  Hz, 1H, CH), 2.06 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 166.3 (C), 149.7 (CH), 143.5 (C), 141.9 (C), 140.3 (C), 139.9 (CH), 138.4 (CH), 135.7 (C), 133.0 (C), 132.7 ( $J_{\text{PTC}} = 26$  Hz, CH), 131.9 ( $J_{\text{PTC}} = 34$  Hz, CH), 130.7 (CH), 130.3 (CH), 129.8 (C), 128.3 (CH), 128.2 (CH), 127.6 (CH), 127.4 (CH), 126.4 (CH), 126.1 ( $J_{\text{PTC}} = 24$  Hz, CH), 125.2 ( $J_{\text{PTC}} = 27$  Hz, CH), 123.8 (CH), 120.2 ( $J_{\text{PTC}} = 33$  Hz, CH), 119.3 ( $J_{\text{PTC}} = 13$  Hz, CH), 22.0 ( $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{29}\text{H}_{22}\text{Cl}_2\text{N}_2\text{Pt}$ : C, 52.42; H, 3.34; N, 4.22; found: C, 52.42; H, 3.41; N, 4.09.

**[PtCl<sub>2</sub>(dtpyH)(tpy)] (3bd).** Pale yellow solid, obtained from **1b** (105 mg, 0.11 mmol), tpyH (92  $\mu\text{L}$ , 0.54 mmol) and  $\text{PhICl}_2$  (65 mg, 0.24 mmol). Yield: 111 mg, 75%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.71 (ddd with satellites,  $J_{\text{HH}} = 5.6, 1.6, 0.7$  Hz,  $J_{\text{PTH}} = 10$  Hz, 1H, CH), 7.98 (s with satellites,  $J_{\text{PTH}} = 25$  Hz, 1H, CH), 7.93 (dd,  $J_{\text{HH}} = 8.2, 1.7$  Hz, 1H, CH), 7.78–7.64 (m, 3H, CH), 7.58 (d,  $J_{\text{HH}} = 8.1$  Hz, 1H, CH), 7.50 (dd,  $J_{\text{HH}} = 7.9, 2.0$  Hz, 1H, CH), 7.47 (d,  $J_{\text{HH}} = 8.1$  Hz, 1H, CH), 7.25 (ddd,  $J_{\text{HH}} = 8.0, 1.8, 0.9$  Hz, 1H, CH), 7.06–7.01 (m, 1H, CH), 6.98 (ddd,  $J_{\text{HH}} = 7.2, 5.6, 1.4$  Hz, 1H, CH), 6.90 (ddd,  $J_{\text{HH}} = 7.8, 1.7, 0.6$  Hz, 1H, CH), 6.79 (dd with satellites,  $J_{\text{HH}} = 7.4, 1.6$  Hz,  $J_{\text{PTH}} = 12$  Hz, 1H, CH), 6.42–6.37 (m, 1H, CH), 6.20 (dd,  $J_{\text{HH}} = 7.8, 2.0$  Hz, 1H, CH), 6.08 (dd with satellites,  $J_{\text{HH}} = 1.5, 0.8$  Hz,  $J_{\text{PTH}} = 37$  Hz, 1H, CH), 2.50 (s, 3H,  $\text{CH}_3$ ), 2.20 (s, 3H,  $\text{CH}_3$ ), 2.07 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR data could not be obtained for this complex because of its very low solubility. Elemental analysis calcd for  $\text{C}_{31}\text{H}_{26}\text{Cl}_2\text{N}_2\text{Pt}$ : C, 53.76; H, 3.78; N, 4.05; found: C, 53.64; H, 3.71; N, 3.93.

**[PtCl<sub>2</sub>(dfppy)(tpy)] (3cd).** Pale yellow solid, obtained from **1c** (150 mg, 0.18 mmol), tpyH (92  $\mu\text{L}$ , 0.54 mmol) and  $\text{PhICl}_2$  (99 mg, 0.36 mmol). Yield: 173 mg, 77%.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 9.77 (ddd with satellites,  $J = 5.5, 1.6, 0.7$  Hz,  $J_{\text{PTH}} \sim 8$  Hz, 1H, CH), 8.29–8.23 (m, 1H, CH), 8.12 (ddd,  $J = 8.2, 7.4, 1.7$  Hz, 1H, CH), 8.07 (dt,  $J = 8.1, 1.0$  Hz, 1H, CH), 7.92–7.83 (m, 2H, CH), 7.63–7.60 (m, 2H, CH), 7.49 (ddd with satellites,  $J = 6.0, 1.6, 0.7$  Hz,  $J_{\text{PTH}} = 33$  Hz, 1H, CH), 7.02 (ddd,  $J = 7.5, 6.1, 1.4$  Hz, 1H, CH), 6.99–6.93 (m, 3H, CH), 6.22 (dd with satellites,  $J = 1.6, 0.7$  Hz,  $J_{\text{PTH}} = 39$  Hz, 1H, CH), 2.12 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 163.9 (dd,  $J_{\text{FC}} = 259, 13$  Hz, C), 162.0 (dd,  $J_{\text{FC}} = 23, 5$  Hz, C), 161.0 (dd,  $J_{\text{FC}} = 261, 13$  Hz, C), 148.4 (s, CH), 146.8 (s, CH), 145.5 (d with satellites,  $J_{\text{FC}} = 9$  Hz,  $J_{\text{PTH}} = 788$  Hz, C), 143.4 (s with satellites,  $J_{\text{PTH}} = 47$  Hz, C), 141.4 (CH), 141.2 (CH), 138.4 (C), 137.1 (s with satellites,  $J_{\text{PTH}} = 741$  Hz, C), 132.6 (s with satellites,  $J_{\text{PTC}} = 37$  Hz, CH), 127.7 (CH), 125.9 (s with satellites,  $J_{\text{PTC}} = 28$  Hz, CH), 125.1–124.7 (m, 2 CH), 124.4 (s with satellites,  $J_{\text{PTC}} = 28$  Hz, CH), 121.0 (s with satellites,  $J_{\text{PTC}} \sim 14$  Hz, CH), 115.3 (d with satellites,  $J_{\text{FC}} = 21$  Hz,  $J_{\text{PTC}} = 21$  Hz, CH), 102.4 (t,  $J_{\text{FC}} = 26$  Hz, CH), 22.0 ( $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (282.4 MHz,

CD<sub>2</sub>Cl<sub>2</sub>): -102.21 (m, 1F), -108.95 (m, 1F); the resonances of two of the quaternary carbon atoms were not observed. Elemental analysis calcd for C<sub>23</sub>H<sub>16</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>Pt: C, 44.24; H, 2.58; N, 4.49; found: C, 44.15; H, 2.77; N, 4.29.

**[PtCl<sub>2</sub>(dfppy)(thpy)] (3ce).** White solid, obtained from **1c** (100 mg, 0.12 mmol), thpyH (104 mg, 0.64 mmol) and PhICl<sub>2</sub> (78 mg, 0.28 mmol). Yield: 127 mg, 86%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.57 (ddd with satellites, *J*<sub>HH</sub> = 5.6, 1.6, 0.8 Hz, *J*<sub>PtH</sub> ~ 14 Hz, 1H, CH), 8.26–8.21 (m, 1H, CH), 8.06 (ddd, *J*<sub>HH</sub> = 8.0, 7.6, 1.6 Hz, 1H, CH), 7.89 (dddd, *J*<sub>HH</sub> = 8.2, 7.5, 1.5, 0.6, 1H, CH), 7.84 (ddd with satellites, *J*<sub>FH</sub> = 8.6, 0.9 Hz, *J*<sub>HH</sub> = 2.4 Hz, *J*<sub>PtH</sub> ~ 36 Hz, 1H, CH), 7.74 (ddd, *J*<sub>HH</sub> = 8.0, 1.3, 0.9, 1H, CH), 7.60 (ddd with satellites, *J*<sub>HH</sub> = 6.1, 1.6, 0.7 Hz, *J*<sub>PtH</sub> ~ 31 Hz, 1H, CH), 7.53 (ddd, *J*<sub>HH</sub> = 7.6, 5.6, 1.3 Hz, 1H, CH), 7.32 (d with satellites, *J*<sub>HH</sub> = 5.0 Hz, *J*<sub>PtH</sub> ~ 6 Hz, 1H, CH), 7.08 (ddd, *J*<sub>HH</sub> = 7.6, 6.0, 1.5, 1H, CH), 6.95 (ddd, *J*<sub>FH</sub> = 12.2, 8.8 Hz, *J*<sub>HH</sub> = 2.4 Hz, 1H, CH), 6.18 (d with satellites, *J*<sub>HH</sub> = 5.0 Hz, *J*<sub>H-Pt</sub> ~ 16 Hz, 1H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 148.4 (CH), 147.2 (CH), 141.6 (CH), 129.8 (CH), 129.0 (CH), 124.8 (CH), 124.7 (CH), 123.4 (CH), 120.3 (CH), 115.9 (CH), 115.8 (CH), 102.7 (t, *J*<sub>FC</sub> = 27 Hz, CH); quaternary carbon atoms were not observed. <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -102.29 (m, 1H), -108.88 (m, 1H). Elemental analysis calcd for C<sub>20</sub>H<sub>12</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>PtS: C, 38.97; H, 1.96; N, 4.54; S, 5.20; found: C, 38.88; H, 2.04; N, 4.60; S, 5.16.

**[PtCl<sub>2</sub>(tpy)]<sub>2</sub> (3dd).** Pale yellow solid, obtained from **1d** (59 mg, 0.07 mmol), tpyH (25 μL, 0.15 mmol) and PhICl<sub>2</sub> (47 mg, 0.17 mmol). Yield: 68 mg, 81%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.77 (ddd with satellites, *J*<sub>HH</sub> = 5.5, 1.7, 0.8 Hz, *J*<sub>PtH</sub> ~ 7 Hz, 1H, CH), 8.10 (ddd, *J*<sub>HH</sub> = 8.2, 7.3, 1.6 Hz, 1H, CH), 8.07–8.04 (m, 1H, CH), 8.04 (dd with satellites, *J*<sub>HH</sub> = 1.7, 0.8 Hz, *J*<sub>PtH</sub> = 26 Hz, 1H, CH), 7.87–7.82 (m, 1H, CH), 7.78 (ddd, *J*<sub>HH</sub> = 8.2, 7.3, 1.4 Hz, 1H, CH), 7.62–7.59 (m, 3H, CH), 7.43 (ddd with satellites, *J*<sub>HH</sub> = 6.0, 1.4, 0.7 Hz, *J*<sub>PtH</sub> = 33 Hz, 1H, CH), 7.24 (ddd, *J*<sub>HH</sub> = 7.9, 1.6, 0.6 Hz, 1H, CH), 6.93 (ddd, *J*<sub>HH</sub> = 7.5, 6.0, 1.5 Hz, 1H, CH), 6.91 (ddd, *J*<sub>HH</sub> = 7.9, 1.6, 0.8 Hz, 1H, CH), 6.20 (dd with satellites, *J*<sub>HH</sub> = 1.6, 0.8 Hz, *J*<sub>PtH</sub> = 40 Hz, 1H, CH), 2.55 (s, 3H, CH<sub>3</sub>), 2.07 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 165.5 (*J*<sub>PtC</sub> = 58 Hz, C), 161.8 (*J*<sub>PtC</sub> = 40 Hz, C), 148.4 (CH), 146.5 (CH), 144.2 (*J*<sub>PtC</sub> = 775 Hz, C), 144.0 (*J*<sub>PtC</sub> = 36 Hz, C), 142.9 (*J*<sub>PtC</sub> = 48 Hz, C), 140.8 (CH), 140.6 (CH), 138.9 (*J*<sub>PtC</sub> = 24 Hz, C), 138.5 (C), 137.0 (*J*<sub>PtC</sub> = 754 Hz, C), 132.9 (*J*<sub>PtC</sub> = 37 Hz, CH), 132.5 (*J*<sub>PtC</sub> = 24 Hz, CH), 127.4 (CH), 127.3 (CH), 125.7 (*J*<sub>PtC</sub> = 29 Hz, CH), 125.5 (*J*<sub>PtC</sub> = 28 Hz, CH), 124.7 (CH), 123.7 (*J*<sub>PtC</sub> = 29 Hz, CH), 121.1 (*J*<sub>PtC</sub> = 34 Hz, CH), 120.8 (CH), 22.5 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>). Elemental analysis calcd for C<sub>24</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>Pt: C, 47.85; H, 3.35; N, 4.65; found: C, 47.70; H, 3.47; N, 4.44.

**[PtCl<sub>2</sub>(tpy)(thpy)] (3de).** Pale yellow solid, obtained from **1d** (100 mg, 0.13 mmol), thpyH (133 mg, 0.82 mmol) and PhICl<sub>2</sub> (83 mg, 0.30 mmol). Yield: 84 mg, 54%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.56 (ddd, *J*<sub>HH</sub> = 5.5, 1.6, 0.8 Hz, 1H, CH), 8.03 (td, *J*<sub>HH</sub> = 7.8, 1.7, 1H, CH), 8.01 (dd with satellites, *J*<sub>HH</sub> = 1.7, 0.9 Hz, *J*<sub>PtH</sub> ~ 29 Hz, 1H, CH), 7.86–7.77 (m, 2H, CH), 7.71 (dt, *J*<sub>HH</sub> = 8.0, 1.0 Hz, 1H, CH), 7.59 (d, *J*<sub>HH</sub> = 7.9 Hz, 1H, CH), 7.54 (ddd with satellites, *J*<sub>HH</sub> = 6.0, 1.3, 0.7 Hz, *J*<sub>PtH</sub> ~ 30 Hz, 1H, CH), 7.51 (ddd, *J*<sub>HH</sub> = 7.6, 5.5, 1.3 Hz, 1H, CH), 7.25 (d, *J*<sub>HH</sub> = 5.0 Hz, 1H, CH), 7.21 (ddd, *J*<sub>HH</sub> = 8.0, 1.5, 0.7 Hz, 1H, CH), 6.98 (ddd, *J*<sub>HH</sub> = 7.9, 6.1, 1.8 Hz, 1H, CH), 6.11 (d with satellites, *J*<sub>HH</sub> = 5.0 Hz, *J*<sub>PtH</sub> ~ 17 Hz, 1H, CH), 2.52 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 165.0 (*J*<sub>PtC</sub> = 59 Hz, C), 157.7 (*J*<sub>PtC</sub> = 32 Hz, C), 148.3 (CH), 146.9 (CH), 143.8 (*J*<sub>PtC</sub> = 36 Hz, C), 141.2 (CH), 140.8 (CH), 139.9 (*J*<sub>PtC</sub> = 770 Hz, C), 139.3 (*J*<sub>PtC</sub> ~ 27 Hz, C), 136.9 (C), 134.8 (*J*<sub>PtC</sub> ~ 795 Hz, C), 133.0 (*J*<sub>PtC</sub> = 26 Hz, CH), 129.4 (*J*<sub>PtC</sub> = 65 Hz, CH), 129.2 (*J*<sub>PtC</sub> = 56 Hz, CH), 127.5 (CH), 125.4 (*J*<sub>PtC</sub> = 28 Hz, CH), 124.0 (*J*<sub>PtC</sub> = 28 Hz, CH), 123.2 (CH), 120.9 (*J*<sub>PtC</sub> = 33 Hz, CH), 120.2 (CH), 22.5 (CH<sub>3</sub>). Elemental analysis calcd for C<sub>21</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>PtS: C, 42.43; H, 2.71; N, 4.71; S, 5.39; found: C, 42.18; H, 2.72; N, 4.64; S, 5.31.

**[PtCl<sub>2</sub>(thpy)(tpy)] (3ed).** To a solution of **2ed** (87 mg, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added PhICl<sub>2</sub> (43 mg, 0.16 mmol) and the mixture was stirred for 10 min. The resulting solution was concentrated under reduced pressure (1 mL) and Et<sub>2</sub>O (20 mL) was added, whereupon a pale-yellow precipitate formed, which was collected by filtration and vacuum-dried to give **3ed**. Yield: 80 mg, 87%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.80 (ddd with satellites, *J*<sub>HH</sub> = 5.5, 1.6, 0.8 Hz, *J*<sub>PtH</sub> ~ 9 Hz, 1H, CH), 8.13-8.09 (ddd, *J*<sub>HH</sub> = 8.1, 7.4, 1.6 Hz, 1H, CH), 8.05 (br d, *J*<sub>HH</sub> = 8.1 Hz, 1H, CH), 7.80 (d, *J*<sub>HH</sub> = 4.9 Hz, 1H, CH), 7.73 (ddd, *J*<sub>HH</sub> = 8.1, 7.4, 1.5 Hz, 1H, CH), 7.66 (d, *J*<sub>HH</sub> = 4.9 Hz, *J*<sub>PtH</sub> = 11 Hz, 1H, CH), 7.62-7.56 (m, 3H, CH), 7.31 (ddd with satellites, *J*<sub>HH</sub> = 6.1, 1.4, 0.7 Hz, *J*<sub>PtH</sub> = 34 Hz, 1H, CH), 6.93 (ddd, *J*<sub>HH</sub> = 7.9, 1.6, 0.7 Hz, 1H, CH), 6.82 (ddd with satellites, *J*<sub>HH</sub> = 7.5, 6.1, 1.5 Hz, *J*<sub>PtH</sub> ~ 8 Hz, 1H, CH), 6.12 (dd with satellites, *J*<sub>HH</sub> = 1.5, *J*<sub>HH</sub> = 0.7 Hz, *J*<sub>PtH</sub> = 39 Hz, 1H, CH), 2.11 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 162.2 (C), 160.6 (C), 148.4 (CH), 146.7 (CH), 145.1 (C), 143.1 (C), 141.2 (CH), 141.0 (CH), 138.4 (C), 136.6 (C), 136.5 (C), 132.9 (*J*<sub>PtC</sub> = 35 Hz, CH), 130.5 (*J*<sub>PtC</sub> = 50 Hz, CH), 130.1 (CH), 127.6 (CH), 125.7 (CH), 124.6 (*J*<sub>PtC</sub> = 12 Hz, CH), 121.9 (*J*<sub>PtC</sub> = 27 Hz, CH), 120.8 (*J*<sub>PtC</sub> = 15 Hz, CH), 120.3 (*J*<sub>PtC</sub> = 30 Hz, CH), 22.1 (CH<sub>3</sub>). Elemental analysis calcd for C<sub>21</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>PtS: C, 42.43; H, 2.71; N, 4.71; S, 5.39; found: C, 42.45; H, 2.58; N, 4.56; S, 5.47.

**[PtCl(dfppy)(tpy)(γ-pic)]OTf (4).** A Carius tube was charged with complex **3cd** (65 mg, 0.10 mmol), AgOTf (25 mg, 0.10 mmol), γ-picoline (10 μL, 0.10 mmol) and 1,2-dichlorobenzene (5 mL) under a N<sub>2</sub> atmosphere and the mixture was stirred at 120 °C for 72 h. The resulting suspension was filtered through Celite. The addition of pentane (20 mL) to the filtrate led to the precipitation of a white solid, which was collected by filtration, recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O and vacuum-dried to give **4** as a white solid. Yield: 57 mg, 65%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.46 (br s, 2H), 8.26 (dt, *J*<sub>HH</sub> = 8.3, 1.9 Hz, 1H), 8.21–8.15 (m, 3H), 8.06 (td, *J*<sub>HH</sub> = 8.0, 1.3 Hz, 1H), 7.99 (d with satellites, *J*<sub>HH</sub> = 6.3 Hz, *J*<sub>PtH</sub> = 31, 1H), 7.92–7.85 (m, 1H), 7.67 (d, *J*<sub>HH</sub> = 8.0 Hz, 1H), 7.60–7.54 (m, 1H), 7.48 (ddd, *J*<sub>HH</sub> = 7.5, 5.9, 1.4 Hz, 1H), 7.40 (d, *J*<sub>HH</sub> = 6.1 Hz, 2H), 7.04-6.95 (m, 2H), 6.18 (s with satellites, *J*<sub>PtH</sub> = 35 Hz, 1H), 2.43 (s, 3H), 2.13 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 164.2 (dd, *J*<sub>FC</sub> = 261, 13 Hz, C), 161.3–161.0 (m, C), 161.0 (dd, *J*<sub>FC</sub> = 262, 13 Hz, C), 154.2 (s, C), 148.8 (s, CH), 148.5 (s, CH), 148.1 (s, CH), 146.8 (s, CH), 144.7 (d, *J*<sub>FC</sub> = 8 Hz, C), 143.8 (s with satellites, *J*<sub>PtC</sub> = 43 Hz, C), 143.3 (s, CH), 142.1 (s, CH), 138.8 (s, C), 133.4 (s with satellites, *J*<sub>PtC</sub> = 37 Hz, CH), 130.0 (s with satellites, *J*<sub>PtC</sub> = 707 Hz, C), 128.9 (s, CH), 128.7 (s, CH), 127.5 (s with satellites, *J*<sub>PtC</sub> = 28 Hz, CH), 126.4 (s with satellites, *J*<sub>PtC</sub> = 25 Hz, CH), 126.0 (s, C), 125.5 (s with satellites, *J*<sub>PtC</sub> ~ 32 Hz, CH), 125.4 (s with satellites, *J*<sub>PtC</sub> ~ 33 Hz, CH), 122.1 (s with satellites, *J*<sub>PtC</sub> ~ 14 Hz, CH), 121.6 (q, *J*<sub>FC</sub> ~ 320 Hz, C), 114.7 (d with satellites, *J*<sub>FC</sub> = 22 Hz, *J*<sub>PtC</sub> ~ 22 Hz, CH), 103.9 (t, *J*<sub>FC</sub> = 27 Hz, CH), 22.1 (s, CH<sub>3</sub>), 21.7 (s, CH<sub>3</sub>). <sup>19</sup>F (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): –78.73 (s, 3F), –100.43 (m, 1F), –106.81 (m, 1F). HRMS (ESI+, *m/z*) calcd for [C<sub>29</sub>H<sub>23</sub>ClF<sub>2</sub>N<sub>3</sub>Pt]<sup>+</sup>: 682.1195; found: 682.1183; error: 1.8 ppm. Elemental analysis calcd for C<sub>30</sub>H<sub>23</sub>ClF<sub>5</sub>N<sub>3</sub>O<sub>3</sub>PtS: C, 43.35; H, 2.79; N, 5.06; S, 3.86; found: C, 43.32; H, 2.61; N, 4.92; S, 3.88.

**mer-[Pt(dfppy)(tpy)<sub>2</sub>]OTf (mer-5cd; mixture of mer isomers).** A Carius tube was charged with **3cd** (80 mg, 0.13 mmol), tpyH (108 μL, 0.64 mmol), AgOTf (66 mg, 0.26 mmol) and 1,2-dichlorobenzene (5 mL) and the mixture was stirred at 120 °C under a N<sub>2</sub> atmosphere for 72 h. The resulting suspension was filtered through Celite. The addition of pentane (20 mL) to the filtrate led to formation of a sticky precipitate, which was washed with Et<sub>2</sub>O (5 × 5 mL) and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). The addition of Et<sub>2</sub>O (15 mL) afforded an off-white solid, which was collected by filtration and vacuum-dried to give **mer-5cd** (37 mg, 33%). The complete NMR data could not be extracted because of the complexity of the signals (see Fig. S14 and S15). HRMS (ESI+, *m/z*) calcd for [C<sub>35</sub>H<sub>26</sub>F<sub>2</sub>N<sub>3</sub>Pt]<sup>+</sup>: 721.1746; found: 721.1734; error: 1.7 ppm.

Elemental analysis calcd for C<sub>36</sub>H<sub>26</sub>F<sub>5</sub>N<sub>3</sub>O<sub>3</sub>PtS: C, 49.66; H, 3.01; N, 4.82; S, 3.68; found: C, 49.46; H, 3.19; N, 4.69; S, 3.48.

**Irradiation of *mer*-5cd.** A solution of the isomer mixture *mer*-5cd (5 mg) in CD<sub>3</sub>CN (0.4 mL) was placed in a quartz NMR tube and irradiated with UV light (310 nm) for 27 h. The resulting NMR spectrum is shown in Fig. S15. HRMS (ESI+, m/z) calcd for [C<sub>35</sub>H<sub>26</sub>F<sub>2</sub>N<sub>3</sub>Pt]<sup>+</sup>: 721.1746; found: 721.1743; error: 0.4 ppm.

***mer*-[Pt(tpy)<sub>3</sub>]OTf (*mer*-5dd).** A Carius tube was charged with 3dd (74 mg, 0.12 mmol), tpyH (51 μL, 0.30 mmol), AgOTf (76 mg, 0.30 mmol) and 1,2-dichlorobenzene (5 mL) and the mixture was stirred at 120 °C under a N<sub>2</sub> atmosphere for 48 h. The resulting suspension was filtered through Celite. The addition of Et<sub>2</sub>O (20 mL) to the filtrate led to the formation of a precipitate, which was collected by filtration, washed with Et<sub>2</sub>O (3 × 4 mL) and vacuum-dried to give *mer*-5dd as white solid (77 mg, 76%). The <sup>1</sup>H NMR data are in agreement with those previously reported.<sup>23</sup>

**[Pt(C<sup>^</sup>N<sup>^</sup>N)(tpyH)]OTf (6).** Complex 3af (115 mg, 0.18 mmol), AgOTf (136 mg, 0.53 mmol) and a degassed solution of tpyH (150 μL, 0.88 mmol) in 1,2-dichloroethane (8 mL) were placed in a Carius tube and the resulting mixture was stirred at 90 °C under a N<sub>2</sub> atmosphere for 48 h. After cooling to room temperature, CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added and the suspension was filtered through Celite. The filtrate was concentrated under reduced pressure (3 mL) and Et<sub>2</sub>O (20 mL) was added, whereupon a solid precipitated, which was filtered off and washed with Et<sub>2</sub>O (3 × 4 mL). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O afforded 6 as a pale-yellow solid. Yield: 37 mg, 23%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.78 (ddd, J<sub>HH</sub> = 6.0, 1.6, 0.7 Hz, 1H, CH), 7.99 (t, J<sub>HH</sub> = 8.0 Hz, 1H, CH), 7.93 (td, J<sub>HH</sub> = 7.8, 1.6 Hz, 1H, CH), 7.86 (d, J<sub>HH</sub> = 8.2 Hz, 2H, CH), 7.81 (dd, J<sub>HH</sub> = 8.3, 1.6 Hz, 1H, CH), 7.73 (ddd, J<sub>HH</sub> = 7.5, 1.3, 0.6 Hz, 1H, CH), 7.61 (td, J<sub>HH</sub> = 7.6, 1.2 Hz, 1H, CH), 7.54–7.50 (m, 3H, CH), 7.41 (td, J<sub>HH</sub> = 7.6, 1.3 Hz, 1H, CH), 7.35–7.31 (m, 2H, CH), 7.28 (m, J<sub>HH</sub> = 8.2 Hz, 2H, CH), 7.23–7.19 (m, 2H, CH), 7.15–7.10 (m, 2H, CH), 7.05 (ddd, J<sub>HH</sub> = 7.6, 1.1, 0.5 Hz, 1H, CH), 6.88 (td, J<sub>HH</sub> = 7.6, 1.4 Hz, 1H, CH), 6.87 (td, J<sub>HH</sub> = 7.6, 1.4 Hz, 1H, CH), 6.64 (ddd, J<sub>HH</sub> = 7.7, 5.4, 1.4 Hz, 1H, CH), 6.55 (ddd, J<sub>HH</sub> = 5.3, 1.6, 0.8 Hz, 1H, CH), 6.27 (ddd, J<sub>HH</sub> = 7.7, 1.2, 0.4 Hz, 1H, CH), 5.78 (dd, J<sub>HH</sub> = 7.8, 1.0 Hz, 1H, CH), 2.42 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 168.2 (C), 162.9 (C), 160.5 (C), 160.4 (C), 154.3 (CH), 152.1 (CH), 145.7 (C), 142.1 (C), 141.8 (C), 140.8 (C), 140.3 (CH), 140.1 (CH), 139.2 (C), 139.0 (C), 138.7 (CH), 136.5 (C), 135.2 (C), 132.6 (CH), 130.9 (CH), 130.3 (CH), 130.2 (CH), 129.9 (CH), 129.3 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 127.9 (CH), 127.6 (CH), 126.5 (CH), 126.2 (CH), 125.6 (CH), 125.1 (CH), 124.8 (CH), 123.3 (CH), 118.7 (CH), 21.8 (CH<sub>3</sub>); the CF<sub>3</sub> resonance was not observed. <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -78.86 (s). HRMS (ESI+, m/z) calcd for [C<sub>40</sub>H<sub>30</sub>N<sub>3</sub>Pt]<sup>+</sup>: 747.2091; found: 747.2086; error: 0.7 ppm. Elemental analysis calcd for C<sub>41</sub>H<sub>30</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>PtS: C, 54.91; H, 3.37; N, 4.69; S, 3.57; found: C, 54.71; H, 3.16; N, 4.61; S, 3.60.

**[Pt(tpy)(tpyH)<sub>2</sub>]OTf (7).** Complex 3af (100 mg, 0.15 mmol), AgOTf (93 mg, 0.36 mmol) and a degassed solution of tpyH (130 μL, 0.76 mmol) in dry 1,2-dichlorobenzene (5 mL) were placed in a Carius tube, and the resulting mixture was stirred at 120 °C under a N<sub>2</sub> atmosphere for 48 h. After cooling to room temperature, CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added and the suspension was filtered through Celite. The filtrate was concentrated under reduced pressure (3 mL) and Et<sub>2</sub>O was added (30 mL). The precipitate was collected by filtration, washed with Et<sub>2</sub>O (3 × 3 mL) and vacuum-dried to give 7 as a pale-yellow solid. Yield: 78 mg, 61%. Using the same procedure, complex 7 was also obtained from 3bd (97 mg, 0.14 mmol), AgOTf (74 mg, 0.29 mmol) and tpyH (0.12 mL, 0.70 mmol). Yield: 57 mg, 48%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.00



(ddd,  $J_{\text{HH}} = 8.6, 7.5, 1.5$  Hz, 1H, CH), 7.93–7.78 (m, 5H, CH), 7.59 (ddd,  $J_{\text{HH}} = 5.6, 1.6, 0.7$  Hz, 1H, CH), 7.56–7.44 (m, 4H, CH), 7.43–7.36 (m, 3H, CH), 7.22–7.10 (m, 5H, CH), 7.06–6.98 (m, 2H, CH), 6.87 (ddd,  $J_{\text{HH}} = 7.5, 6.0, 1.5$  Hz, 1H, CH), 6.18 (s with satellites,  $J_{\text{PtH}} = 41$  Hz, 1H, CH), 2.41 (s, 6H, CH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 168.3$  (C), 161.1 (C), 160.9 (C), 154.5 (CH), 151.7 (CH), 149.0 (CH), 142.8 (C), 141.7 (C), 141.1 (C), 141.0 (C), 140.5 (CH), 139.5 (C), 139.5 (CH), 139.0 (CH), 136.5 (C), 136.1 (C), 133.6 ( $J_{\text{PtC}} = 56$  Hz, CH), 130.0 (2CH), 129.8 (2CH), 129.2 (2CH), 129.1 (2CH), 127.4 ( $J_{\text{PtC}} = 63$  Hz, CH), 127.1 ( $J_{\text{C-Pt}} = 32$  Hz, CH), 126.2 (CH), 125.0 (CH), 124.9 (CH), 124.5 ( $J_{\text{PtC}} = 40$  Hz, CH), 123.4 ( $J_{\text{PtC}} = 35$  Hz, CH), 120.1 ( $J_{\text{PtC}} = 43$  Hz, CH), 22.1 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>); the CF<sub>3</sub> resonance was not observed. <sup>19</sup>F (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -78.88$  (s). HRMS (ESI+, m/z) calcd for [C<sub>36</sub>H<sub>32</sub>N<sub>3</sub>Pt]<sup>+</sup>: 701.2247; found: 701.2260; error: 1.8 ppm. Elemental analysis calcd for C<sub>37</sub>H<sub>32</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>PtS: C, 52.23; H, 3.79; N, 4.94; S, 3.77; found: C, 52.20; H, 3.84; N, 4.71; S, 3.83.

### X-ray structure determinations

Single crystals of **2af**, **2ed**, **3af**, **3bd**, **3cd**, **4**·Et<sub>2</sub>O and **6**·0.5CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray diffraction were obtained by the liquid-liquid diffusion method from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. In the cases of **2af** or **2ed**, crystallization required the presence of an excess ppyH or tpyH, respectively. Numerical details are presented in the ESI (Tables S1 and S2). The data were collected on a Bruker D8 QUEST diffractometer with monochromated Mo-*K* $\alpha$  radiation performing  $\omega$  scans (**2af**, **3bd** and **3cd**) or  $\varphi$  and  $\omega$  scans (rest of complexes). The structures were solved by dual methods<sup>48</sup> and refined anisotropically on  $F^2$  using the program SHELXL-2018 (G. M. Sheldrick, University of Göttingen).<sup>49</sup> Methyl hydrogens were included as part of rigid idealized methyl groups allowed to rotate but not tip; other hydrogens were included using a riding model. *Special features of refinement*: In **3bd**, there is a poorly resolved region of residual electron density that could not be adequately modelled and therefore the program SQUEEZE,<sup>50</sup> which is part of the PLATON system, was employed to mathematically remove the effects of the solvent; the void volume per cell was 335 Å<sup>3</sup>, with a void electron count per cell of 79; this additional solvent was not taken into account when calculating derived parameters such as the formula weight, because its nature was uncertain. In **6**·0.5CH<sub>2</sub>Cl<sub>2</sub>, the triflate anion is disordered over two positions, approximately 54:46%.

### Computational methods

DFT calculations were carried out with the Gaussian 09 package,<sup>51</sup> using the hybrid B3LYP functional<sup>52,53</sup> together with the 6-31G\*\*<sup>54,55</sup> basis set for the light atoms and the LANL2DZ<sup>56</sup> basis set and effective core potential for the Pt atom. All geometry optimizations were carried out without symmetry restrictions, using "tight" convergence criteria and "ultrafine" integration grid. Vertical excitation energies were obtained from TDDFT calculations at the ground-state optimized geometries. Triplet state geometry optimizations were carried out following a reported strategy.<sup>57</sup> The solvent effect (CH<sub>2</sub>Cl<sub>2</sub>) was accounted for in all cases by using the integral equation formalism variant of the polarizable continuum solvation model (IEFPCM).<sup>58</sup> All the optimized structures were confirmed as minima on the potential energy surface by performing frequency calculations (zero imaginary frequencies). Natural spin densities were obtained from natural population analyses using the NBO 5.9 program.<sup>59</sup>

### Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

We thank the Spanish Ministerio de Economía y Competitividad (CTQ2015-69568-P), Fundación Séneca (19890/GERM/15) and Ministerio de Ciencia, Innovación y Universidades (PGC2018-100719-BI00) for financial support. Á. Vivancos and D. Poveda thank Fundación Séneca for a Saavedra Fajardo Fellowship (20398/SF/17) and a predoctoral fellowship (20725/FPI/18), respectively.

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