

Synthesis and characterization of new Pd(II) and Pt(II) complexes with 3-substituted 1-(2-pyridyl) imidazo[1,5-a]pyridine ligands.

Questa è la versione Post print del seguente articolo:

*Original*

Synthesis and characterization of new Pd(II) and Pt(II) complexes with 3-substituted 1-(2-pyridyl) imidazo[1,5-a]pyridine ligands / Stoccoro, S., Pishedda, S., Zucca, A., Sciortino, G., Ortu, F., Clarksonf, G.J.. - In: DALTON TRANSACTIONS. - ISSN 1477-9226. - 50:(2021), p. 4859. [10.1039/d1dt00546d]

*Availability:*

This version is available at: 11388/276478 since: 2023-02-02T22:18:37Z

*Publisher:*

*Published*

DOI:10.1039/d1dt00546d

*Terms of use:*

Chiunque può accedere liberamente al full text dei lavori resi disponibili come "Open Access".

*Publisher copyright*

note finali coverpage

(Article begins on next page)

# Dalton Transactions

An international journal of inorganic chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Stoccoro, S. Pischedda, A. Zucca, G. Sciortino, F. Ortu and G. Clarkson, *Dalton Trans.*, 2021, DOI: 10.1039/D1DT00546D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

# 1 Synthesis and characterization of new Pd(II) and Pt(II) complexes with 3-substituted 1-(2-pyridyl)imidazo[1,5-*a*]pyridine ligands

2  
3  
4 Sara Pischedda,<sup>a,b</sup> Sergio Stoccoro,<sup>a,b</sup> \* Antonio Zucca,<sup>a,b</sup> Giuseppe Sciortino,<sup>c</sup> Fabrizio Ortu<sup>d,e</sup> and  
5 Guy J. Clarkson<sup>f</sup>

- 6  
7 a) Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, via Vienna 2, 07100  
8 Sassari, Italy  
9 b) Consorzio Interuniversitario Reattività Chimica e Catalisi (CIRCC), Bari, Italy  
10 c) Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007  
11 Tarragona, Spain  
12 d) School of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK  
13 e) Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9 PL,  
14 UK  
15 f) Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL,  
16 UK

17 \* E-mail: stoccoro@uniss.it  
18  
19

## 20 Abstract

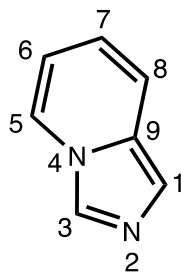
21 Several palladium(II) and platinum(II) complexes (**1-20**) of general formula [M(L<sup>n</sup>)(X)(Y)] [M = Pd,  
22 X = Y = Cl (**1-Cl-4-Cl**), X = Y = OAc (**1-OAc-4-OAc**); M = Pt: X = Y = Cl (**5-8**); M = Pd, X = Cl,  
23 Y = CH<sub>3</sub> (**9-12**); M = Pt, X = Cl, Y = CH<sub>3</sub> (**13-16**) or X = Y = CH<sub>3</sub> (**17-20**); n = 1-4] have been  
24 synthesized by reaction of different Pd(II) and Pt(II) derivatives with various 3-substituted 1-(2-  
25 pyridyl)-imidazo[1,5-*a*]pyridines; *i.e.* L<sup>n</sup>=1-(2-pyridyl)-3-arylimidazo[1,5-*a*]pyridine (aryl = Phenyl,  
26 L<sup>1</sup>; 2-*o*-Tolyl, L<sup>2</sup>; Mesityl, L<sup>3</sup>) and 1-(2-pyridyl)-3-benzylimidazo[1,5-*a*]pyridine (L<sup>4</sup>). Detailed  
27 spectroscopic investigation (including IR, mono- and bi-dimensional <sup>1</sup>H NMR) and elemental  
28 analysis has been performed for all these species, allowing their complete characterization. L<sup>n</sup> act as  
29 *N,N*-bidentate ligands and coordinates the metal centers in a chelate fashion through the pyridyl (N<sub>py</sub>)  
30 and the pyridine-like nitrogen atom of the imidazo[1,5-*a*]pyridine group (N<sub>im</sub>). The X-ray structural  
31 analysis performed on two of Pd(II) and three Pt(II) complexes, namely [Pd(L<sup>2</sup>)(CH<sub>3</sub>)Cl] (**10**),  
32 [Pd(L<sup>3</sup>)(CH<sub>3</sub>)Cl] (**11**) and [Pt(L<sup>1</sup>)Cl<sub>2</sub>] (**5**), [Pt(L<sup>4</sup>)Cl<sub>2</sub>] (**8**), [Pt(L<sup>2</sup>)(CH<sub>3</sub>)Cl] (**14**) confirmed the  
33 spectroscopic and analytical data. Finally DFT studies unveiled the structural reasons behind the  
34 inertia of the synthesised compounds toward metalation, identified as the higher angle steric strain in  
35 comparison with the analogous bipyridine complexes.  
36

## 37 Introduction

View Article Online  
DOI: 10.1039/D1DT00546D

38 The coordination chemistry of heavy  $d^8$  transition metals (*e.g.* Ir(I), Pd(II), Pt(II), Au(III)) is  
39 dominated by the use of bidentate nitrogen donors as supporting ligands, wherein 2,2'-bipyridines  
40 and 1,10-phenanthrolines are the most important examples.<sup>1</sup> In particular, the extraordinary  
41 coordination properties of 2,2'-bipyridines in metal-catalyzed reactions<sup>2</sup> have led to a myriad of  
42 applications in a variety of fields, including macromolecular chemistry,<sup>3</sup> supramolecular chemistry,<sup>4</sup>  
43 materials chemistry,<sup>5</sup> photochemistry<sup>6</sup> and electrochemistry.<sup>7</sup>

44 Following our continuous interest in the study of the reactivity of bidentate nitrogen ligands,<sup>8</sup> we  
45 decided to investigate the coordinating behaviour of a series of aromatic *N*-heterocyclic ligands  
46 containing the imidazo[1,5-*a*]pyridine skeleton (Figure 1)<sup>9</sup> *i.e.* 1-(2-pyridyl)-3-arylimidazo[1,5-*a*]  
47 pyridines and 1-(2-pyridyl)-3-benzylimidazo[1,5-*a*]pyridine.

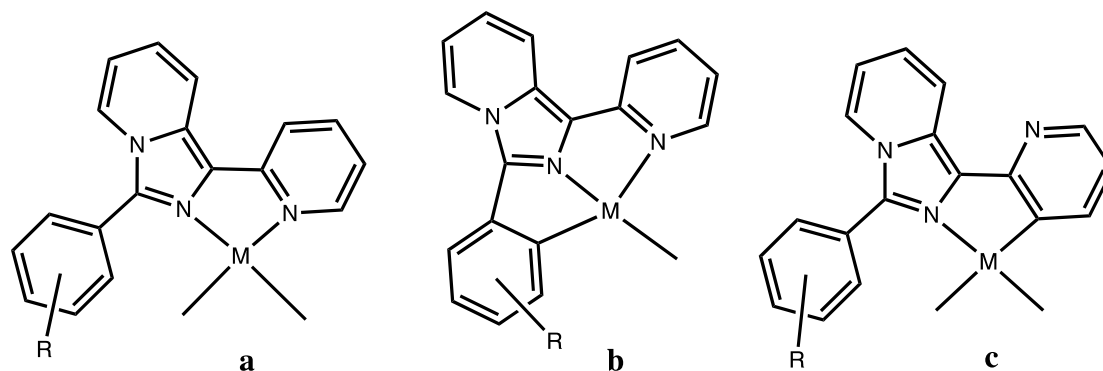


49  
50 **Fig. 1.** Imidazo[1,5-*a*]pyridine skeleton:

51 the atom numbering adopted throughout the text

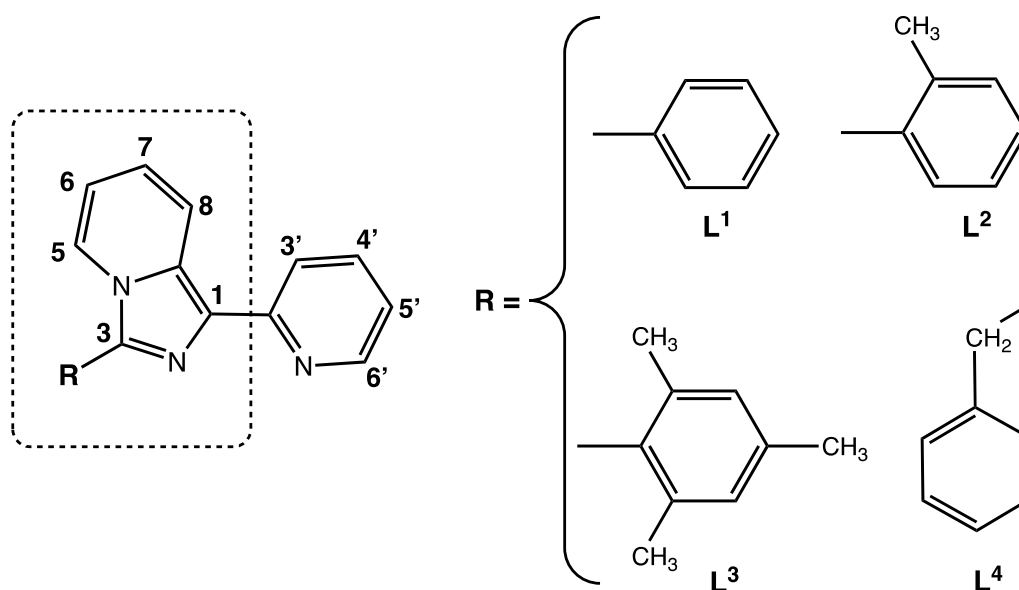
52  
53 The wealth of nitrogen heterocycles offer many intriguing possibilities for the development of  
54 bidentate nitrogen donors for the synergic tuning of structural and physicochemical properties of  
55 resulting complexes. In particular, 1-(2-pyridyl)imidazo[1,5-*a*]pyridines have emerged as an  
56 attractive new class of ligands, owing to their ability to act as bidentate donors by employing their  
57 pyridyl unit in conjunction with a fused imidazole.<sup>10</sup> Heterocycles containing the imidazo[1,5-*a*]  
58 pyridine skeleton possess unique photophysical properties<sup>11</sup> and have potential applications in the  
59 field of OLEDs<sup>12</sup> and organic thin-layer field-effect transistors (FETs).<sup>13</sup> Different 1-(2-  
60 pyridyl)imidazo[1,5-*a*]pyridines have been coordinated to transition metals to produce highly  
61 luminescent complexes containing Re(I),<sup>14</sup> Zn(II),<sup>15,13</sup> Ag(I),<sup>16</sup> Cd(II),<sup>17</sup> Ru(II) and Os(II)<sup>18</sup> metal  
62 centers. Furthermore, the coordination of these complexes with small organic molecules often  
63 produces a significant effect on their biological activities.<sup>19</sup> The coordinating behaviour of these  
64 ligands with  $d^8$  ions of transition metals, like Pd(II) and Pt(II), is to our knowledge unexplored.  
65 These ligands resemble 6-substituted 2,2'-bipyridines and we intended to verify the possibility that in  
66 addition to the typical N-N chelating behaviour (Figure 2a), cyclometallated complexes could also be

67 obtained by activation of a C-H bond of the aryl substituent in the 3-position (Figure 2b) or via  
 68 rollover cyclometallation resulting from the activation of a C-H bond of the pyridyl substituent  
 69 (Figure 2c).<sup>20</sup>



72 **Fig. 2.** Sketch of possible targets.

73  
 74  
 75 With this idea in mind, we synthesized a series of ligands containing the heterocyclic imidazo[1,5-  
 76 *a*]pyridine core, owing also to its huge biological and medicinal applications (Figure 3).<sup>19-21</sup> We also  
 77 selected several substituents to tune the steric protection around the metal center and allow for  
 78 different C-H activation possibilities involving either C(sp<sup>2</sup>)-H or C(sp<sup>3</sup>)-H bonds, thus leading to the  
 79 potential formation of 5- and 6-membered metallacycles. Therefore, we selected aryls [phenyl (Ph,  
 80 L<sup>1</sup>), *o*-tolyl (*o*-Tol, L<sup>2</sup>), mesityl (Mes, L<sup>3</sup>)], together with a benzylic group (CH<sub>2</sub>Ph, L<sup>4</sup>) as  
 81 substituents.



82 **Fig. 3.** Ligands synthesized and used in this work.

84 **Results and discussion**

85

86 **Synthesis and characterization of the ligands**

87 The ligands 1-(2-pyridyl)-3-arylimidazo[1,5-*a*]pyridine **L<sup>n</sup>** (n= 1-3) (Figure 3) were readily  
 88 synthesized, in good yields, by reacting suitable aromatic aldehydes with 2,2'-dipyridylketone and  
 89 ammonium acetate in hot acetic acid, using minor modifications to the published procedures.<sup>22</sup> On  
 90 the other hand, the ligand 1-(2-pyridyl)-3-benzylimidazo[1,5-*a*]pyridine, **L<sup>4</sup>**, was synthesized  
 91 following a different procedure due to the instability of the corresponding aliphatic imine which is  
 92 formed during the synthesis.<sup>23</sup>

93 The structure of the ligands was assessed by <sup>1</sup>H NMR spectroscopy: multi-dimensional NMR  
 94 experiments were employed to assign all the proton signals (see **Table 1**).

96

**Table 1.** <sup>1</sup>H NMR selected data of **L<sup>n</sup>** in CDCl<sub>3</sub>

<b>L<sup>n</sup></b>	<b>H<sub>8</sub></b>	<b>H<sub>6</sub>'</b>	<b>H<sub>5</sub></b>	<b>H<sub>3</sub>'</b>	<b>H<sub>4</sub>'</b>	<b>H<sub>5</sub>'</b>	<b>H<sub>6</sub></b>	<b>H<sub>7</sub></b>	<b>Others</b>
L <sup>1</sup>	8.70; d	8.64; d	8.26; d	8.24; d	7.72; td	7.10; dd	6.92; dd	6.65; td	
L <sup>2</sup>	8.71; d	8.64; d	7.64; d	8.23; d	7.70; t	7.09; dd	6.60; t	6.93; t	2.26; s, <b>CH<sub>3</sub></b>
L <sup>3</sup>	8.94; d	8.89; d	7.61; d	8.48; d	7.95; td	7.33; dd	6.82; dd	7.17; t	2.62; s, [3H] <b>CH<sub>3</sub></b> para. 2.27; s, [6H] <b>CH<sub>3</sub></b> ortho
L <sup>4</sup>	8.62; d	8.60; d	7.59; d	8.17; d	7.71; td	7.07; dd	6.52; dd	6.84; t	4.51; s, <b>CH<sub>2</sub></b>

97

98

99 For example, the interpretation of <sup>1</sup>H NMR spectra of **L<sup>n</sup>** in CDCl<sub>3</sub> is far from trivial; the existence  
 100 of three different spin systems involving two sets of protons and a variable number of protons  
 101 depending on the 3-substituent was clearly identified by 2D NMR techniques (COSY, and NOE, see  
 102 the Supporting Information).<sup>24</sup> For **L<sup>1</sup>** these spin systems include 4 (●), 4 (○), and 5 (◆) protons  
 103 respectively (Figure 4). This information however was not sufficient to unequivocally assign all  
 104 signals in relation to the proposed molecular structure.

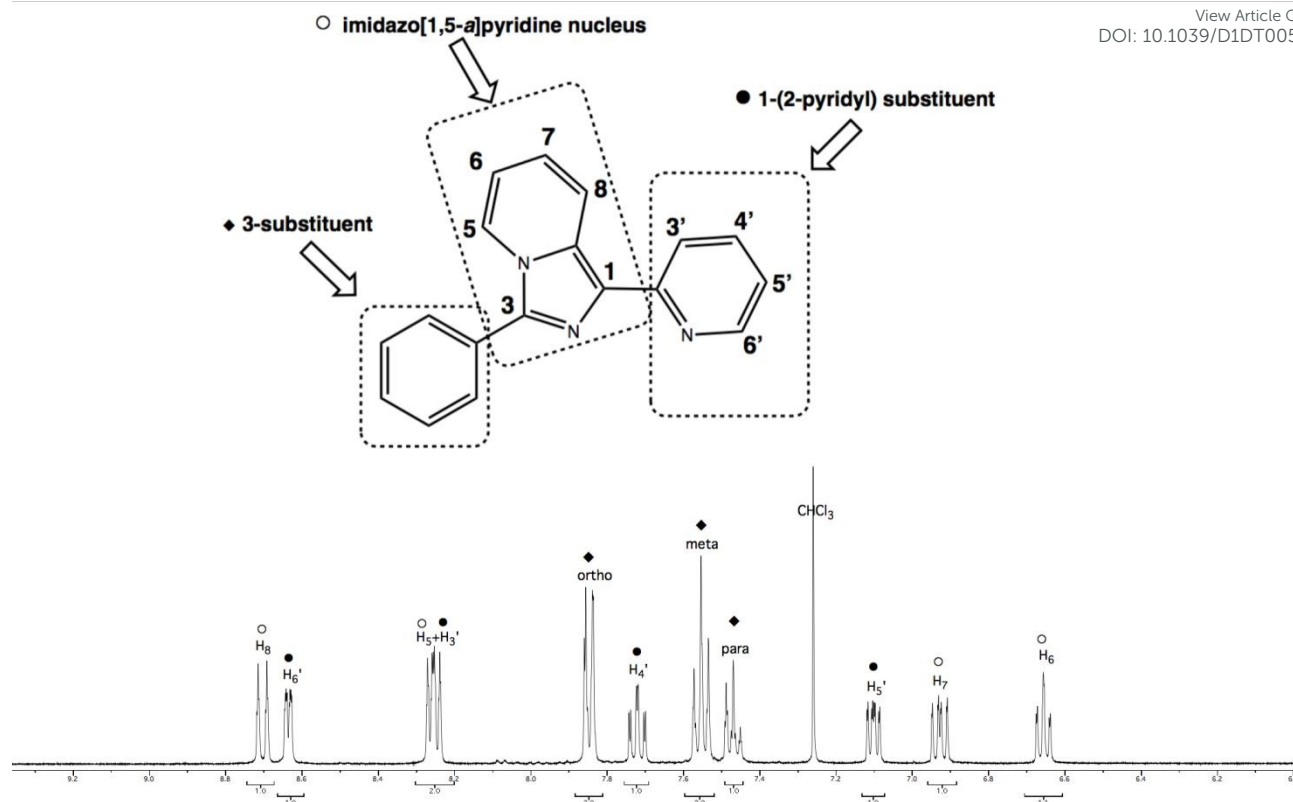


Fig. 4. Spin systems of ligand  $L^1$

In the  $^1\text{H}$  NMR spectrum of  $L^1$  the signal resonating at lower fields has been attributed to the proton  $\text{H}_8$ ; this is an anomalous chemical shift, especially compared to the signal of the proton  $\text{H}_5$  and considering also the proximity to the nitrogen atom in 4-position of the imidazo[1,5-*a*] pyridine skeleton. We believe this unusual shift is due to the interaction of the proton  $\text{H}_8$  with the nitrogen atom of the pyridyl substituent in 1-position (Figure 5).

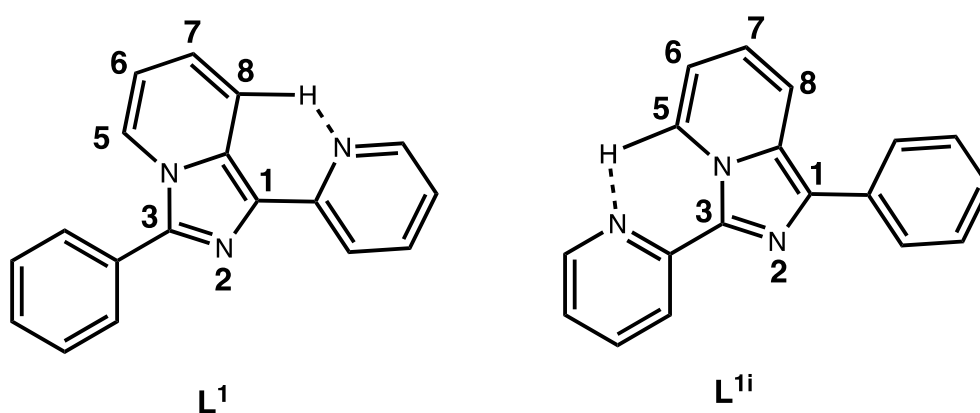


Fig. 5. Long-range  $\text{N}\cdots\text{H}$  interaction in  $L^1$  and  $L^{1i}$

117 To confirm this observation we synthesized the isomer of **L**<sup>1</sup> (1-phenyl-3-(2-pyridyl)imidazol[5-  
 118 *a*]pyridine), **L**<sup>1i</sup>, in which the positions of the 2-pyridyl and the phenyl substituents have been  
 119 exchanged (Figure 5).<sup>25</sup> Gratifyingly, in the <sup>1</sup>H NMR spectrum of **L**<sup>1i</sup> the most deshielded proton is  
 120 proton H5, which is in agreement with the presence of a long-range N...H interaction (assignments  
 121 based on COSY and NOESY spectra, Figure S1).

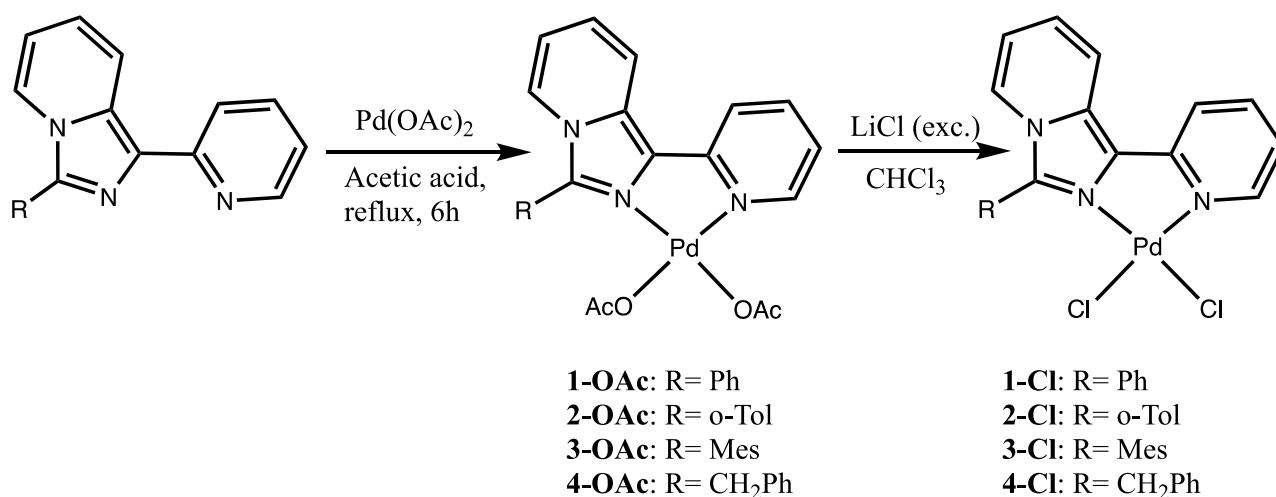
122

123

### 124 *Synthesis and characterization of the complexes [Pd(L<sup>n</sup>)X<sub>2</sub>] (X=Cl, OAc) and [Pt(L<sup>n</sup>)Cl<sub>2</sub>]*

125 The reaction of **L**<sup>1-4</sup> with Pd(OAc)<sub>2</sub> led to the formation of adducts [Pd(L<sup>n</sup>)(OAc)<sub>2</sub>] (**1-OAc**: n = 1; **2-**  
 126 **OAc**: n = 2; **3-OAc**: n = 3; **4-OAc**: n = 4), followed by anion exchange with LiCl to yield the adducts  
 127 [Pd(L<sup>n</sup>)Cl<sub>2</sub>] (**1-Cl**: n = 1; **2-Cl**: n = 2; **3-Cl**: n = 3; **4-Cl**: n = 4). In all complexes the ligands act as  
 128 classic chelating N<sup>^</sup>N donors and spectroscopic investigation confirms the presence in solution of the  
 129 PdCl<sub>2</sub> adducts, which was also further corroborated *via* elemental analysis (Scheme 1).

130



131

132

133 **Scheme 1.** Synthesis of PdCl<sub>2</sub> adducts *via* metathesis of Pd(OAc)<sub>2</sub> adducts with LiCl.

134

135 In the case of **1-Cl** the formation of a cyclometallated species can be ruled out by spectroscopic  
 136 analysis, despite the employment of reaction conditions which normally afford activation of the  
 137 C(sp<sup>2</sup>)-H bond in the *ortho* position of phenyl substituents.<sup>26</sup> In the <sup>1</sup>H NMR spectrum of **1-Cl** the  
 138 number of signals and their integral values are in perfect agreement with the proposed formulation.  
 139 The most salient features are: 1) a significant upfield shift of the H8 signal upon complexation ( δ  
 140 7.82 ppm vs δ 8.70 ppm in the free ligand); 2) a downfield shift of the signal related to the proton  
 141 H6' (δ 9.00 ppm vs δ 8.61 ppm in the free ligand).

The alterations of the substituents in ligands **L**<sup>2</sup>, **L**<sup>3</sup> and **L**<sup>4</sup> offer different possibilities for the potential formation of cyclometalated species. With **L**<sup>2</sup> and **L**<sup>3</sup> ligands we wanted to exploit the possibility of the C-H activation in the methyl group in the *ortho* position, thereby leading to the formation of a 6-membered metallacycle featuring less ring strain with respect to analogous 5-membered cycles expected with **L**<sup>1</sup>. However, this would involve a less favourable activation of C(sp<sup>3</sup>)-H bonds compared to a C(sp<sup>2</sup>)-H activation predicted in the case of the phenyl substituent. On the other hand, the employment of ligand **L**<sup>4</sup> could lead to the formation of a 6-membered metallacycle by activating an aromatic C(sp<sup>2</sup>)-H bond. Nevertheless, in every case only the adducts [Pd(**L**<sup>n</sup>)Cl<sub>2</sub>] were isolated and even trace amounts of the cyclometalated derivatives could not be detected by <sup>1</sup>H NMR analysis. In the <sup>1</sup>H NMR spectra all signals have been assigned; noticeably, the proton H6' of the pyridyl ring is significantly deshielded, due to the presence of the chloride bound to the metal (Table 2).<sup>27</sup> The proposed structures were confirmed by CHN analyses.

**Table 2.** <sup>1</sup>H NMR data in CD<sub>2</sub>Cl<sub>2</sub> of [Pd(**L**<sup>n</sup>)Cl<sub>2</sub>] (**1-Cl** ÷ **4-Cl**)

#	H6'	H5'	H4'	H3'	H8	H7	H6	H5	H <sup>ar</sup>	Other
<b>1-Cl</b>	9.10	7.22	7.85	7.98	7.91	7.33	6.89	7.97	7.65	
<b>2-Cl</b>	9.25	7.41	8.03	7.85	7.95	7.41	6.88	7.55	7.55- 7.41	2.21 ortho CH <sub>3</sub>
<b>3-Cl</b>	9.26	7.33	8.01	7.43	7.93	7.33	6.87	7.84	7.08	2.41, para CH <sub>3</sub> ; 2.03 ortho CH <sub>3</sub> [6H]
<b>4-Cl</b>	9.27	7.27	7.97	7.89	7.89	7.27	6.88	7.77	7.34	4.44 CH <sub>2</sub>

To confirm the lack of cyclometalated species, in the two steps process (see Scheme 1), the corresponding acetate derivatives **1-OAc**, **2-OAc**, **3-OAc** and **4-OAc** were also isolated and characterized. In the <sup>1</sup>H NMR spectra of these species (Table 3) different chemical shifts for methyl protons of the acetate are observed, likely due to the inequivalence of the two nitrogen donors. The methyl signal at higher fields can be confidently assigned as the acetate ligand in *trans* with respect to the pyridyl moiety (N<sub>py</sub>): by arranging itself perpendicularly to the metal plane, the aromatic ring of the aryl group imparts a more effective shielding on the vicinal acetate group compared to the effect exerted on the other acetate ligand *trans* to the imidazolyl nitrogen (N<sub>im</sub>). This effect is less pronounced in the case of **4-OAc** owing to the presence of the benzylic CH<sub>2</sub> spacer.

**Table 3.** <sup>1</sup>H NMR data in CDCl<sub>3</sub> of [Pd(**L**<sup>n</sup>)(OAc)<sub>2</sub>] (**1-OAc** ÷ **4-OAc**)

#	H6'	H5'	H4'	H3'	H8	H7	H6	H5	H <sup>ar</sup>	Other
<b>1-OAc</b>	8.12	7.24	7.98	7.80	7.91	7.29	6.86	7.85	7.67- 7.60	1.99 CH <sub>3</sub> (OAc); 1.13 CH <sub>3</sub> (OAc);

<b>2-OAc</b>	8.14	7.25	7.98	7.51	7.89	7.31	6.86	7.79	7.50-7.40	2.18	ortho CH <sub>3</sub> (OAc); 1.98 CH <sub>3</sub> (OAc); 1.11 CH <sub>3</sub> (OAc);
<b>3-OAc</b>	8.14	7.30	7.98	7.40	7.89	7.24	6.85	7.77	7.04	2.35	para CH <sub>3</sub> ; 2.09 ortho CH <sub>3</sub> [6H]; 1.98 CH <sub>3</sub> (OAc); 1.13 CH <sub>3</sub> (OAc);
<b>4-OAc</b>	8.07	7.16	7.92	7.74	7.84	7.16	6.77	7.84	7.35-7.23	4.60	CH <sub>2</sub> ; 2.14 CH <sub>3</sub> (OAc); 1.89 CH <sub>3</sub> (OAc);

166

167

168

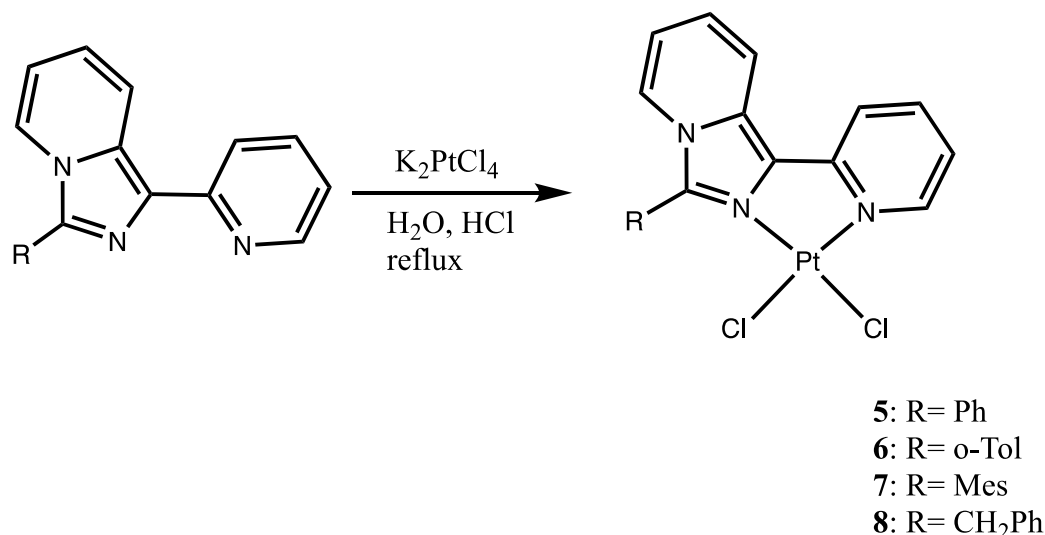
169

170

171

172

In order to further investigate the inertness towards metalation, we prepared the analogous Pt(II) from the reaction of ligands **L**<sup>1-4</sup> with K<sub>2</sub>PtCl<sub>4</sub> in a 1:1 ratio, in water and HCl under reflux (Scheme 2). These experimental conditions were chosen as they previously led to the formation of cyclometalated species when 6-phenyl-2,2'-bipyridine was employed as a ligand.<sup>28</sup> However, also in this case only the corresponding Pt(II) adducts [Pt(**L**<sup>n</sup>)Cl<sub>2</sub>] (**5**: n = 1; **6**: n = 2; **7**: n = 3; **8**: n = 4) could be isolated:



173

174

175

176

177

178

179

180

181

182

**Scheme 2.** Synthesis of PtCl<sub>2</sub> adducts.

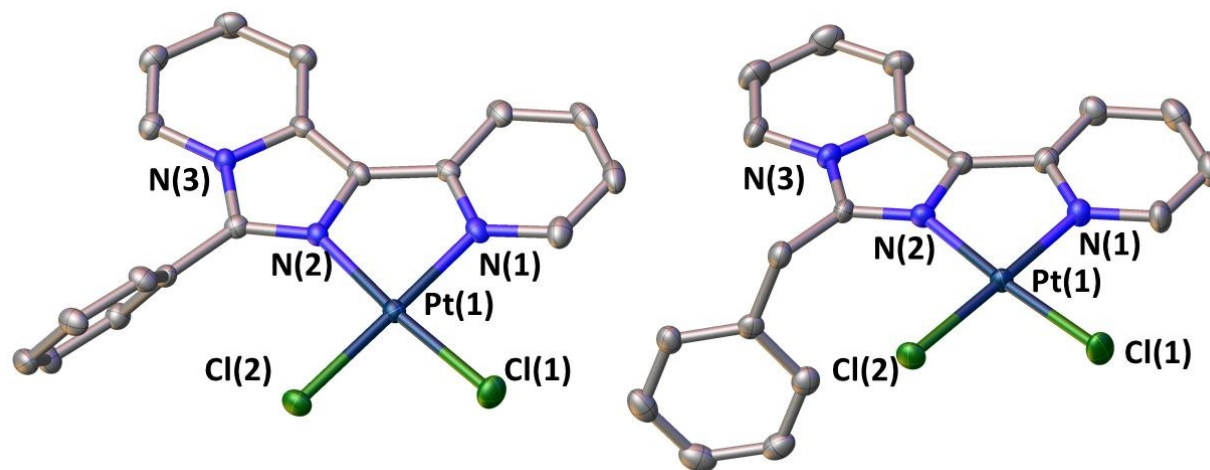
These were fully characterised with analytical and spectroscopic techniques; elemental analyses also support the formation of the adducts **5-8** and the absence of cyclometalated species. The <sup>1</sup>H NMR data is also in complete agreement with the proposed formulation. In particular, in all cases the H6 'proton signals are more deshielded than those of the corresponding palladium complexes most likely due to the greater electronegativity of platinum.<sup>29</sup> The coupling constant <sup>3</sup>J<sub>Pt-H</sub> confirms the successful coordination of the pyridyl nitrogen to the platinum atom. In compound **7** the methyl groups in the *ortho* are isochronous, like in the case of the analogous Pd complex **3-Cl**.

**Table 4.**  $^1\text{H}$  NMR data in  $\text{CDCl}_3$  of  $[\text{Pt}(\text{L}^n)\text{Cl}_2]$  (**5** - **8**)View Article Online  
DOI: 10.1039/D1DT00546D

#	H6'	H5'	H4'	H3'	H8	H7	H6	H5	H <sup>ar</sup>	Other
<b>5</b>	9.51 (36 Hz)*	7.33	8.05	7.84	7.95	7.33	6.92	7.84	7.66	
<b>6</b>	9.63 (34 Hz)	7.62	8.07	7.86	7.96	7.62	6.91	7.62	7.62-7.28	2.22 ortho $\text{CH}_3$
<b>7</b>	9.63 (37 Hz)	7.31	8.07	7.87	7.97	7.37	6.91	7.43	7.07	2.42, para $\text{CH}_3$ ; 2.03, ortho $\text{CH}_3$ [6H]
<b>8</b>	9.39 (38 Hz)	7.51	8.22	8.22	8.33	7.22	7.12	8.33	7.51-7.22	5.41 $\text{CH}_2$

\*in brackets  $^3J_{\text{Pt-H}}$ 

X-ray quality crystals of compounds **5** and **8** were obtained by slow diffusion of di-isopropyl ether into a dichloromethane solution at room temperature, which lead to the identification of the molecular structure of both species (Figure 6). **5** and **8** crystallise in monoclinic  $P2_1/n$  and  $P2_1/c$  respectively, and both display square planar geometry around the Pt centre [**5**:  $\Sigma_{\angle} = 359.95(14)$ ; **8**:  $\Sigma_{\angle} = 360.0(2)^\circ$ ], featuring a pyridyl-imidazopyridine ligand which acts as a bidentate donor [**5**: Pt1–N1 = 2.020(2) Å, Pt1–N2 = 2.023(2) Å; **8**: Pt1–N1 2.029(2) Å, Pt1–N2 = 2.028(3) Å] and the metal centre perfectly placed on the mean plane calculated between the four donor atoms [Pt...mean l.s. plane: **5**: 0.0320(8) Å; **8**: 0.0109(11) Å]. Two chloride ions are bound to the metal centre in *cis* mutual position to complete the coordination sphere [**5**: Pt1–Cl1 = 2.2896(8) Å, Pt1–Cl2 = 2.2869(8) Å **8**: Pt1–Cl1 = 2.2883(9) Å, Pt1–Cl2 = 2.2961(11) Å] (see Table S1).

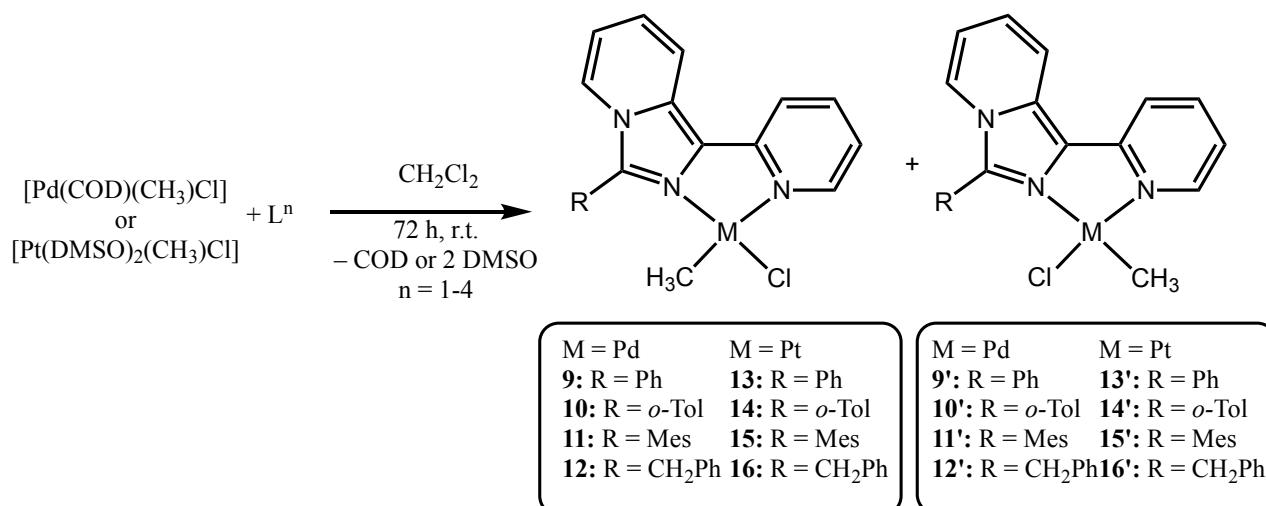


**Figure 6.** Solid state structure of **5** (left) and **8** (right) with selective atom labelling and thermal ellipsoids set at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond length and angles for **5**: Pt(1)–Cl(1) 2.2896(8) (Å); Pt(1)–Cl(2) 2.2869(8) (Å); Pt(1)–N(1) 2.8020(2) (Å); Pt(1)–N(2) 2.023(2) (Å); N(1)–Pt(1)–N(2) 80.60(9)°. Selected bond length and angles for **8**: Pt(1)–Cl(1) 2.2883(8) (Å); Pt(1)–Cl(2) 2.2961(10) (Å); Pt(1)–N(1) 2.028(3) (Å); Pt(1)–N(2) 2.029(3) (Å); N(1)–Pt(1)–N(2) 80.44(11)°.

203 **Synthesis of chloro(methyl) derivatives of Pd(II) and Pt(II),  $[M(L^n)(CH_3)Cl]$** View Article Online  
DOI: 10.1039/D1DT00546D

204 With the intent to further expand the coordination chemistry of these new ligands sets, we targeted  
 205 the synthesis of heteroleptic adducts of Pd and Pt by employing the organometallic starting materials  
 206  $[Pd(COD)(CH_3)Cl]$  and  $[Pt(DMSO)_2(CH_3)Cl]$ . These were reacted with the free ligands  $L^n$  (Scheme  
 207 3), affording the new heteroleptic organometallic derivatives  $[Pd(L^n)(CH_3)Cl]$  (**9**:  $n=1$ ; **10**:  $n=2$ ; **11**:  
 208  $n=3$ ; **12**:  $n=4$ ) and  $[Pt(L^n)(CH_3)Cl]$  (**13**:  $n=1$ ; **14**:  $n=2$ ; **15**:  $n=3$ ; **16**:  $n=4$ ).

209



210 **Scheme 3:** Synthesis of heteroleptic organometallic Pd and Pt complexes **9-16** and isomers **9'-16'**.

211

212 All the resulting complexes are 1:1 adducts in which the nitrogen ligands act as a chelating donor.  
 213 Due to the inequivalence of the two nitrogen donors and the planar square geometry typical of the  
 214 Pd(II) and Pt(II) systems, two geometric isomers are expected: one with the methyl group in *trans* to  
 215 pyridyl-N ( $N_{py}$ ) the other with the methyl group in *trans* to imidazolyl-N ( $N_{im}$ ) (Scheme 3).  $^1H$  NMR  
 216 studies (Table 5) reveal, in the case of most Pd complexes, there is a marked preference for the pyridyl  
 217 donor ( $N_{py}$ ) to bind *trans* to the methyl group (major isomers: **9-11**). The minor isomers, **9'-11'**, are  
 218 also formed in smaller quantities, with the methyl groups positioned in *trans* with respect to the  
 219 imidazolyl donor ( $N_{im}$ ). In the  $^1H$  NMR spectra of **9-11**, the signals related to the Pd-CH<sub>3</sub> and H6'  
 220 pyridine protons are very diagnostic and indicate the formation of the proposed structures. In the  
 221 major isomers  $\delta$ (Pd-Me) occurs in the range 1.05-0.35 ppm and the H6' are markedly downfield  
 222 shifted due to the proximity of the coordinated halide. In contrast, in the case of complex  
 223  $[Pd(L^4)(CH_3)Cl]$  the major isomer in solution is that with the methyl group in *trans* to  $N_{im}$  (**12'**),  
 224 most likely because of steric effects (*vide infra*).

225

226

**Table 5.** <sup>1</sup>H NMR selected data in CDCl<sub>3</sub> of [Pd(L<sup>n</sup>)(CH<sub>3</sub>)Cl] (**9** ÷ **12**) (**9'** ÷ **12'**)View Article Online  
DOI: 10.1039/D1DT00546D

#	H6'	CH <sub>3</sub> of the aryllic substituent in 3 (L <sup>2</sup> , L <sup>3</sup> ) or CH <sub>2</sub> (L <sup>4</sup> )	Pd-CH <sub>3</sub>	%
<b>9</b>	9.11 d		0.35 s	85
<b>9'</b>	8.51d		1.04 s	11
<b>10</b>	9.13 d	2.17 s [3H] <i>ortho</i>	0.39 s	95
<b>10'</b>	8.51 d	2.25 s	1.00 s	5
<b>11</b>	9.18 d	2.02 s [6H] <i>ortho</i> ; 2.41 s [3H] <i>para</i>	0.39 s	98
<b>11'</b>	8.55 d	2.03 s [6H] <i>ortho</i> ; 2.38 s [3H] <i>para</i>	1.01 s	2
<b>12'</b>	8.56 d	5.15 s [2H]	1.17 s	90
<b>12</b>	9.23 d	5.36 s [2H]	1.26 s	10

227

228

229

230

231

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

248

249

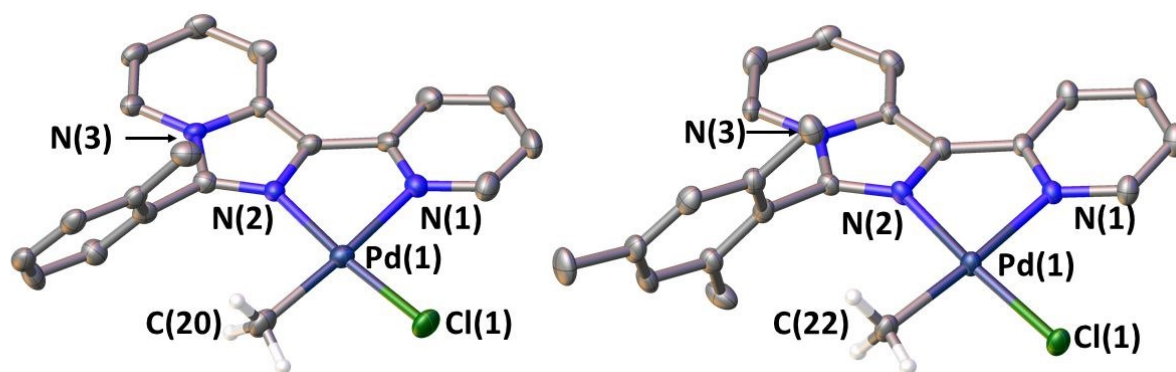
250

The assignment of the two isomers' signals can be inferred from: 1) the chemical shift of the H6' proton, which is very deshielded compared to the free ligand, due to the presence of chloride bound to the metal center; 2) the chemical shift of the methyl ligand bound to the Pd centre, which is shielded by the proximity of the phenyl substituent that is located almost perpendicularly to the metal plane, thus shielding the methyl protons. In the case of complex [Pd(L<sup>1</sup>)(CH<sub>3</sub>)Cl] a third species is also present (ca. 4%), which we assigned as the dichloride analogue **1**, occurring from the reaction of **9** with the chlorinated solvent.<sup>30</sup> The same trend can be reported for the other complexes, **10** and **11** with an increase in the percentage of the isomer prevailing (methyl ligand *trans* to pyridyl ring) with the increase in the steric hindrance of the substituent (Table 5).

The <sup>1</sup>H NMR spectrum of complex with L<sup>4</sup> displays a behaviour in stark contrast with our previous observations. The main stereoisomer is the one with the methyl in *trans* to the imidazo nitrogen (N<sub>im</sub>) (**12'**), as it can be easily deduced by the chemical shift of the H6' proton (see Table 6). Because of the benzylic CH<sub>2</sub> spacer, the shielding effect operated by the aromatic ring of the substituent on the Pd-CH<sub>3</sub> is not as effective as that observed in the cases seen above (δ 1.26 ppm vs δ 1.17 ppm).

X-ray quality crystals of compounds **10** and **11** were obtained by slow diffusion of di-isopropyl ether into a dichloromethane solution at room temperature (Figure 7). Compound **10** crystallises in the monoclinic *P2<sub>1</sub>/c*, whilst **11** crystallises in the triclinic *P-1*. Both compounds displays square planar geometries around the Pd centre [**10**: Σ<sub>z</sub> = 360.0(4)°; **11**: Σ<sub>z</sub> = 359.9(3)°], with the pyridyl-imidazopyridine ligands acting as bidentate donors similarly to what observed previously for **5** and **8** [**10**: Pd1-N1 = 2.143(5) Å; Pd1-N2 = 2.067(5) Å; **11**: Pd(1)-N(1) = 2.055(3) Å; Pd(1)-N(3) = 2.148(4) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms [Pt1...mean l.s. plane: **10**: 0.039(2) Å; **11**: 0.049(2) Å]. In **10**, the methyl carbon C(20) is in the *trans* position with respect to pyridyl nitrogen N(3) [Pt1-C20 = 2.114(5) Å], whilst chloride ion

251 Cl(1) is positioned in *trans* to the imidazolyl nitrogen N(1) [Pt1–Cl1 = 2.295(2) Å]. The same  
 252 coordination motif is observed in **11** [Pd(1)–Cl(1) = 2.3064(13) Å; Pd(1)–C(22) = 2.049(5) Å; Cl(1)–  
 253 Pd(1)–C(22A) = 89.22(14)°] (see Table S2). The isomers **10'** and **11'** were also detected as disordered  
 254 components in the solid state analysis of **10** and **11**: **10'** has an occupancy of approximately 15%,  
 255 whilst **11'** accounts for only 5% of the crystallographic model (see SI). These observations are in  
 256 agreement with the spectroscopic data. Unfortunately, due to the low occupancy of the minor  
 257 components (**10'** and **11'**), it is not possible to offer any detailed structural analysis.



259  
 260 **Figure 7.** Solid state structure of **10** (left) and **11** (right) with selective atom labelling and thermal  
 261 ellipsoids set at 50% probability level. Hydrogen atoms have been omitted for clarity with the  
 262 exception of those belonging to methyl groups C(20) and C(22). Selected bond length and angles for  
 263 **10**: Pd(1)–Cl(1) 2.300(2) (Å); Pd(1)–C20(2) 2.069(9) (Å); Pd(1)–N(1) 2.147(4) (Å); Pd(1)–N(2)  
 264 2.068(4) (Å); N(1)–Pd(1)–N(2) 79.67(15)°. Selected bond length and angles for **11**: Pd(1)–Cl(1)  
 265 2.3064(12) (Å); Pd(1)–C(22) 2.049(5) (Å); Pd(1)–N(1) 2.148(3) (Å); Pd(1)–N(2) 2.055(3) (Å); N(1)–  
 266 Pd(1)–N(2) 78.94(12)°.

269 In the case of Pt(II) analogue complexes [Pt(L<sup>n</sup>)(CH<sub>3</sub>)Cl] (**13**: n = 1; **14**: n = 2; **15**: n = 3; **16**:  
 270 n = 4) were obtained and characterised; the most significant data, obtained from the analysis of the  
 271 <sup>1</sup>H NMR spectra, are reported in **Table 6**.

272 The Pt chloro(methyl)derivatives were obtained in good yield, with the exception of the complex  
 273 obtained with L<sup>4</sup> (**16**). Also in this case all compounds were thoroughly characterized with analytical  
 274 and spectroscopic methods. The interpretation of the <sup>1</sup>H NMR spectra of the platinum complexes (see  
 275 Table 6) is simpler than palladium complexes due to the coupling of the protons with the NMR active  
 276 <sup>195</sup>Pt nucleus. In this case, the Pt–H coupling allowed us to identify with certainty the prevailing  
 277 geometric isomer in solution *i.e.* the one with N<sub>py</sub> in *trans* to methyl group (**13–15**). Accordingly, the  
 278 corresponding <sup>3</sup>J<sub>Pt-H</sub> shown in Table 6 for the H6' signal of the pyridine ring should be very small,  
 279 owing to the strong *trans*-influence the methyl ligand. In our case it was not possible to resolve these

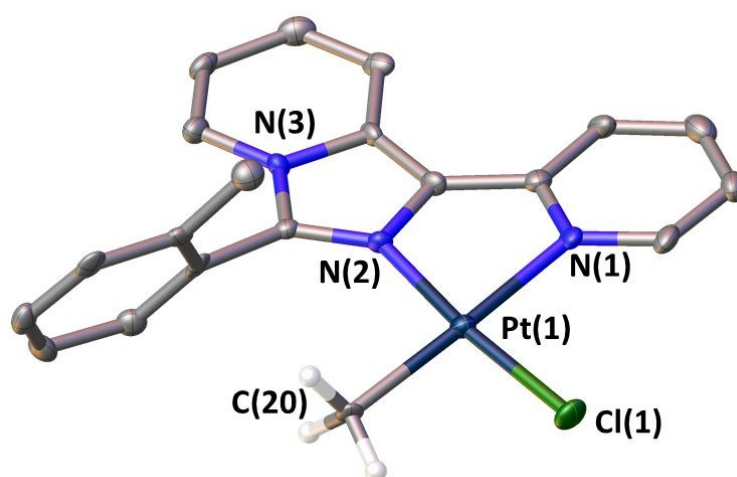
280 signals due to the high intensity of the field to which the  $^1\text{H}$  NMR spectra were registered (due to  
 281 Chemical Shift Anisotropy, CSA). In the case of the minor isomer (*i.e.* with the methyl in *trans* to  
 282  $\text{N}_{\text{im}}$ ) the value of  $^3\text{J}_{\text{Pt-H}}$  for the same proton ( $\text{H6}'$ ) was found to be approximately 60 Hz, which is in  
 283 agreement with the presence in the *trans* position of a ligand with low *trans*-influence, such as a  
 284 chloride. Also in this case, the chemical shift of the methyl ligand is considerably shielded by the ring  
 285 current of the aryl substituent and resonates at  $\delta = 1$  ppm, as already observed for the corresponding  
 286 Pd complexes. When ligand  $\text{L}^4$  was employed, complex  $\mathbf{16}'$  was isolated in poor yield, featuring the  
 287 methyl group in *trans* to  $\text{N}_{\text{im}}$ . In this case, the chemical shift of methyl is shifted to  $\delta = 1.25$  ppm with  
 288 a coupling constant of approximately 80 Hz. This observation highlights the effect of the benzylic  
 289  $\text{CH}_2$  spacer in attenuating the shielding effect imparted by the aromatic ring of the substituent.

**Tables 6.**  $^1\text{H}$  NMR selected data in  $\text{CDCl}_3$  of  $[\text{Pt}(\text{L}^n)(\text{CH}_3)\text{Cl}]$  (**13**, **14**, **15**; **13'**, **14'**, **16'**)

#	$\text{H6}'$	$\text{CH}_3$ of the aryl substituent in <b>3</b> ( $\text{L}^2$ , $\text{L}^3$ ) or $\text{CH}_2$ ( $\text{L}^4$ )	Pt- $\text{CH}_3$	%
<b>13</b>	9.49 d; (not resolved)*		0.51 s; $^2\text{J}_{\text{Pt-H}} = 78.1$ Hz	80
<b>13'</b>	8.96 d; (ca. 60 Hz)		1.21 s; $^2\text{J}_{\text{Pt-H}} = 72.2$ Hz	20
<b>14</b>	9.37d; (not resolved)*	2.04 s [3H] <i>ortho</i>	0.39 s; $^2\text{J}_{\text{Pt-H}} = 77.5$ Hz	89
<b>14'</b>	8.84 d; (ca. 62 Hz)	2.12 s; [3H] <i>ortho</i>	1.09 s; $^2\text{J}_{\text{Pt-H}} = 71.7$ Hz	11
<b>15</b>	9.44 d; (not resolved)	2.02 s [6H] <i>ortho</i> ; 2.19 s [3H] <i>para</i>	0.52 s; $^2\text{J}_{\text{Pt-H}} = 80.0$ Hz	ca.100
<b>16'</b>	9.04 d $^3\text{J}_{\text{Pt-H}} = 60.0$ Hz	5.30 s [2H]	1.25 s; $^2\text{J}_{\text{Pt-H}} = 80.1$ Hz	100

\*in brackets  $^3\text{J}_{\text{Pt-H}}$

291  
 292  
 293 X-ray quality crystals of compound **14**, were obtained by slow diffusion of di-isopropyl ether into a  
 294 dichloromethane solution at room temperature (Figure 8). Compound **14** crystallises in the  
 295 monoclinic  $P2_1/c$  and displays an analogous coordination motif to **10** and **11**, with square planar  
 296 geometry around the Pt centre [ $\Sigma_{\text{L}} = 360.0(6)^\circ$ ; Pt1-N1 = 2.110(4) Å; Pt1-N2 = 2.026(4) Å;  
 297 Pt1...mean l.s. plane = 0.043(2) Å]; the Pt-N<sub>pyridyl</sub> distance is elongated with respect to dichloride  
 298 analogues **5** and **8** [2.020(2) Å and 2.028(3) Å respectively] owing to the methyl carbon C(20)  
 299 positioned in *trans* with respect to pyridyl nitrogen N(1) [Pt1-C20 = 2.068(11) Å], whilst the Pt-Cl  
 300 bond is *trans* to the imidazo nitrogen N(2) is of similar magnitude to the other complexes described  
 301 in this report [Pt1-Cl1 = 2.217(8) Å] (see Table S2). Also in this case the isomer **14'** is present in the  
 302 crystallographic model, with an occupancy of approximately 15% (see SI).



**Fig. 8.** Molecular structure of **14** with ellipsoids set at 50% probability level. Hydrogens have been omitted for clarity with the exception of those belonging to methyl group C(20).

#### *Synthesis of dimethyl derivatives of Pt(II), [M(L<sup>n</sup>)(CH<sub>3</sub>)<sub>2</sub>]*

Finally, we synthesised and fully characterised a series of dimethyl derivatives of formula [Pt(L<sup>n</sup>)(CH<sub>3</sub>)<sub>2</sub>] (**17**: n = 1; **18**: n = 2; **19**: n = 3; **20**: n = 4), by reacting the precursor [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>] with free ligand L<sup>n</sup>. Reactions were carried out initially in dichloromethane, but the solvent was changed to acetone in order to prevent activation of the chlorinated solvents as previously reported in the literature.<sup>30</sup> Indeed the <sup>1</sup>H NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> showed evidence of a mixture of products consisting of the expected adduct, [Pt(L<sup>n</sup>)(CH<sub>3</sub>)<sub>2</sub>], together with a mixture of complexes obtained by oxidative addition of dichloromethane *i.e.* [Pt(L<sup>n</sup>)(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>Cl)Cl].<sup>30</sup> So clean adducts were obtained by operating in acetone, and their formation was confirmed *via* <sup>1</sup>H NMR studies carried out in deuterated acetone (Table 7).

**Table 7.** <sup>1</sup>H NMR in acetone-d<sub>6</sub> of [Pt(L<sup>n</sup>)(CH<sub>3</sub>)<sub>2</sub>] (**17** ÷ **20**)

#	H6'	CH <sub>3</sub> of the aryl substituent in 3 (L <sup>2</sup> -L <sup>3</sup> ) or CH <sub>2</sub> (L <sup>4</sup> )	Pt-CH <sub>3</sub>
<b>17</b>	9.04 d; (ca. 24 Hz)*		0.76 s; <sup>3</sup> J <sub>Pt-H</sub> = 90.0 Hz 0.26 s; <sup>3</sup> J <sub>Pt-H</sub> = 89.4 Hz
<b>18</b>	9.03 d; (ca. 24 Hz)	2.21 s [3H] CH <sub>3</sub> ortho	0.75 s; <sup>3</sup> J <sub>Pt-H</sub> = 88.5 Hz 0.24 s; <sup>3</sup> J <sub>Pt-H</sub> = 90.6 Hz
<b>19</b>	9.04 d; (ca. 24 Hz)	2.38 s [3H] CH <sub>3</sub> para; 2.01 s [6H] CH <sub>3</sub> ortho	0.77 s; <sup>3</sup> J <sub>Pt-H</sub> = 88.1 Hz 0.28 s; <sup>3</sup> J <sub>Pt-H</sub> = 88.5 Hz
<b>20</b>	9.04 d; (ca. 24 Hz)	4.90 s, [2H]	1.10 s; <sup>3</sup> J <sub>Pt-H</sub> = 87.0 Hz 0.91 s; <sup>3</sup> J <sub>Pt-H</sub> = 87.9 Hz

\* in brackets <sup>3</sup>J<sub>Pt-H</sub>

320 The elemental analyses and the spectroscopic characterization of these complexes are in agreement  
 321 with the reported stoichiometry. The ligands act as a chelating bidentate with the two methyls in *trans*  
 322 to the two different nitrogen atoms, N<sub>py</sub> and N<sub>im</sub>. The corresponding signals are easily distinguishable  
 323 thanks to the chemical shift, being the one at higher fields the methyl in *trans* to the pyridine ring due  
 324 to the screen operated by the substituent in 3-position of the imidazo-pyridine skeleton. This effect  
 325 is less pronounced for the complex obtained with **L<sup>4</sup>** (**20**). The <sup>3</sup>J<sub>Pt-H</sub> of the protons belonging to the  
 326 two methyl ligands coordinated to the Pt centre are not very different from each other, highlighting a  
 327 very similar *trans*-influence of the two types of nitrogen donor groups. Surprisingly, the <sup>3</sup>J<sub>Pt-H</sub>  
 328 coupling constants of the H6' protons can be accurately measured, unlike the platinum chloro(methyl)  
 329 complexes seen previously (Table 7).

330

331

### 332 *Theoretical analysis*

333 As discussed above with this series of ligands, contrary to what was observed in our previous works,<sup>8i</sup>  
 334 cyclometalation can't be realized. Taking advantage of the X-Ray structure of the [Pt(L<sup>n</sup>)Cl<sub>2</sub>] series  
 335 and to understand the nature of this phenomenon we performed a theoretical prediction of the Gibbs  
 336 energy associated with the metalation of the four Pt adducts ([Pt(L<sup>n</sup>)Cl<sub>2</sub>]<sub>aq</sub> → [Pt(L<sup>n</sup>-H)Cl]<sub>aq</sub> +  
 337 HCl<sub>aq</sub>) comparing the values with the thermodynamics of the complex formed by the similar ligand  
 338 6-(1-phenylbenzyl)-2,2'-bipyridine (bipy). In Table S5 is summarized a comparison of X-Ray and  
 339 DFT (M06/6-311g(d,p)/SDD+f[ECP]) selected parameters, the little deviations demonstrate that the  
 340 selected DFT level of theory guarantees accurate performances in the structural prediction of this  
 341 kind of complexes. Furthermore the method appear robust and was successfully applied in literature  
 342 for high accuracy energy prediction of transition metal complexes.<sup>31</sup>

343 The results summarized in Table 8 clearly show that the hypothetical reaction is associated, for all  
 344 the ligands, with ΔG<sub>aq</sub> values considerably higher respect the homologous reaction of [Pt(**bipy**)Cl<sub>2</sub>].  
 345 Particularly ΔΔG<sub>aq</sub> values ranging from 7.10 to 17.31 kcal·mol<sup>-1</sup> highlight thermodynamics inertia of  
 346 the metallatation for the [Pt(L<sup>n</sup>)Cl<sub>2</sub>] series.

347

**Table 8.** Theoretical relative ΔG<sub>aq</sub> calculations for the cyclometallation reaction of the synthesized adducts: [Pt(L<sup>n</sup>)Cl<sub>2</sub>]<sub>aq</sub> → [Pt(L<sup>n</sup>-H)Cl]<sub>aq</sub> + HCl<sub>aq</sub>.

Complex	ΔΔG <sub>gas</sub> <sup>[a]</sup>	ΔΔG <sub>aq</sub> <sup>[a],[b]</sup>
[Pt(L <sup>1</sup> -H)Cl]	21.15	17.31
[Pt(L <sup>2</sup> -H)Cl]	16.84	13.41

$[(\text{Pt}(\text{L}^3\text{-H})\text{Cl})]$	14.08	11.12
$[(\text{Pt}(\text{L}^4\text{-H})\text{Cl})]$	13.97	7.10

View Article Online  
DOI: 10.1039/D1DT00546D

[a] Values in  $\text{kcal}\cdot\text{mol}^{-1}$  referred to the value obtained for the bypi complex taken as a zero,  $\text{ref}^{\text{8i}}$ . [b] Gibbs free energy computed with the following formulae:  $\Delta G_{\text{aq}} = \Delta G_{\text{gas}} + \Delta G_{\text{sol}}([\text{Pt}(\text{L}^n\text{-H})\text{Cl}]) - \Delta G_{\text{sol}}([\text{Pt}(\text{L}^n)\text{Cl}_2]) + \Delta G_{\text{sol}}(\text{HCl}) + RT\ln V$ .

348

349

350

351

352

353

354

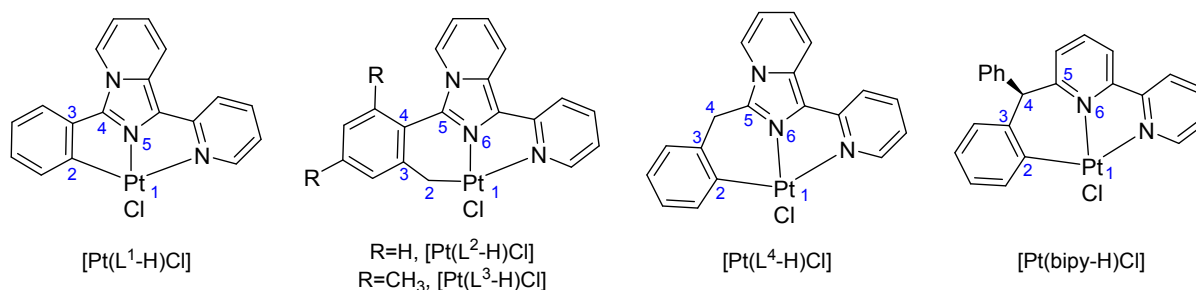
355

356

357

An accurate structural analysis of the hypothetical cyclometallated complexes unveils the reasons behind the high  $\Delta\Delta G_{\text{aq}}$  associated with the cyclometallation. The 5-member and 6-member rings formed by the ligands  $\text{L}^{1-4}$  presents a high angle steric strain in comparison with the characterized bipyridine complex. As it can be seen in Table 9, the mean of the deviation from the ideal angles ranges from  $4.35^\circ$  to  $8.51^\circ$  for the ligands synthesized in this work versus  $2.94^\circ$  computed for the stable complex  $[\text{Pt}(\text{bipy}\text{-H})\text{Cl}]$ . In addition, the distances  $\text{Pt}(\text{II})\text{-N}$  play a critical role, in fact the cyclometallation forces these bonds to become smaller respect to the ideal values increasing the potential energy of the compounds.

**Table 9.** Selected bond lengths and bond angles on the formed ring in cyclometallation reaction. In parenthesis is reported the absolute deviation from the ideal value in angstrom and degrees respectively.



	$[\text{Pt}(\text{L}^1\text{-H})\text{Cl}]$ [a]	$[\text{Pt}(\text{L}^2\text{-H})\text{Cl}]$ [a]	$[\text{Pt}(\text{L}^3\text{-H})\text{Cl}]$ [a]	$[\text{Pt}(\text{L}^4\text{-H})\text{Cl}]$ [a]	$[\text{Pt}(\text{bipy}\text{-H})\text{Cl}]$ [a]
<b>Angles</b> [b],[c]					
5-member ring		6-member ring	6-member ring	6-member ring	6-member ring
1-2-3	112.05 (7.95)	116.88 (7.38)	116.44 (6.94)	123.61 (3.61)	120.27 (0.27)
2-3-4	114.18 (5.82)	125.44 (5.44)	124.73 (4.73)	127.76 (7.76)	122.70 (2.70)
3-4-5	113.93 (6.07)	120.29 (0.29)	118.29 (1.71)	118.64 (9.14)	115.51 (6.01)
4-5-1(6)	126.28 (6.28)	123.28 (3.28)	123.22 (3.22)	126.37 (6.37)	119.34 (0.66)
5-1(6)-2(1)	73.56 (16.44)	130.11 (10.11)	128.79 (8.79)	131.17 (11.17)	124.30 (4.30)
6-1-2	--	90.36 (0.36)	89.28 (0.72)	92.09 (2.09)	93.67 (3.67)
Mean dev.	8.51	4.48	4.35	6.69	2.94

#### Distances

[b],[c]

Pt(II)-N(1)	1.933 (0.090)	1.978 (0.045)	1.980 (0.043)	1.982 (0.041)	2.041 (0.018)
Pt (II)-N(3)	2.313 (0.293)	2.198 (0.178)	2.211 (0.191)	2.196 (0.176)	2.154 (0.134)
<i>Mean dev.</i>	<i>0.192</i>	<i>0.112</i>	<i>0.117</i>	<i>0.109</i>	<i>0.076</i>

Article Online  
DOI: 10.1039/D1DT00546D

[a] DFT computed structural data from this work. [b] Angles in degrees. [c] Distances in Å.

358

## 359 Conclusions

360 In this work we wanted to test the behaviour of four ligands of the imidazo[1,5a]pyridine series with  
 361 Pd(II) and Pt(II) in order to compare the results with those obtained with 2,2'-bipyridine ligands.  
 362 Although this study with these metal ions is a novelty for these ligands, the result is that only neutral  
 363 adducts have been obtained in which the ligand acts as an N,N chelating: in no case has activation of  
 364 CH bonds been obtained as was obtained instead in the case of 2,2'-bipyridine ligands. The theoretical  
 365 study performed on the Pt(II) series suggest that the high angle steric strain of the 5- and 6-member  
 366 rings formed by the ligands **L**<sup>1-4</sup> as well as the deviation from ideal Pt(II)-N distances could be  
 367 responsible of the thermodynamics inertia of these complexes toward cyclometallation.

## 368 Author Contributions

369 Conceptualization, S.S.; Formal analysis, S.S., S.P and A.Z.; Funding acquisition, A.Z., S.S.;  
 370 Investigation, S.P., S.S., A.Z., F.O. and G.C.; Methodology, S.S., S.P. A.Z. and F.O.; Resources,  
 371 A.Z., and S.S.; Software, G.S., F.O. and G.C.; Supervision, S.S., F.O.; Writing—original draft, S.S.,  
 372 S.P., F.O. and G.S.; Writing—review & editing, S.S., S.P., A.Z., F.O., G.S. and G.C.; All authors  
 373 have read and agreed to the published version of the manuscript.

## 375 Conflicts of interest

376 The authors declare no conflict of interest. The funders had no role in the design of the study; in the  
 377 collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to  
 378 publish the results.

## 380 Acknowledgments

381 Financial support from Università degli Studi di Sassari is gratefully acknowledged (“*Fondo di*  
 382 *Ateneo per la Ricerca 2020*”: S.S. and A.Z.). F.O. would like to acknowledge Dr. Chris Muryn, the  
 383 X-ray service at the Department of Chemistry, University of Manchester, and the Engineering and  
 384 Physical Sciences Research Council (Grant EP/K039547/1) for support.

385

386 **Experimental section**View Article Online  
DOI: 10.1039/D1DT00546D

387 All the solvents were purified and dried according to standard procedures.<sup>32</sup> The starting complexes  
388  $[\text{Pd}(\text{COD})(\text{CH}_3)\text{Cl}]^{33}$ , *trans*- $[\text{Pt}(\text{DMSO})_2(\text{CH}_3)\text{Cl}]^{34}$  and *cis*- $[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]^{26a,35}$  were  
389 synthesized according to literature. Elemental analyses were performed with a Perkin-Elmer  
390 elemental analyzer 240B at the Department of Chemistry and Pharmacy of the University of Sassari.  
391 FT-IR spectra were registered with a Jasco FT-IR-480 Plus spectrometer. <sup>1</sup>H spectra were recorded  
392 with a Bruker Avance III 400 spectrometer operating at 400.0 MHz. Chemical shifts are given in ppm  
393 relative to internal TMS for <sup>1</sup>H, J values are given in Hz. Two-dimensional <sup>1</sup>H COSY and NOESY  
394 spectra were performed by means of standard pulse sequences.

395

396

397 **Synthesis of the ligands**398 **L<sup>1</sup> (3-phenyl-1-(pyridin-2-yl)imidazo[1,5-*a*]pyridine)**

399 To a solution of bis(2-pyridyl)ketone (0.9209 g; 5.00 mmol) in acetic acid (30 ml) were added  
400 benzaldehyde (1.01 ml; 10 mmol) and ammonium acetate (1.9010 g; 25 mmol). The pale yellow  
401 solution was refluxed under inert atmosphere for 5 h. The solution was then put in a mixture of  
402 water/ice (250 ml), extracted with dichloromethane, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to  
403 small volume. The product was purified with a chromatographic column using a mixture of ethyl  
404 acetate and n-hexane (8:2). The solution was concentrated to a small volume and n-hexane was added  
405 to give a yellow precipitate (**L<sup>1</sup>**). Yield: 0.6647 g (49%).

406 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: 8.70 (d, 1H, **H<sup>8</sup>**); 8.64 (d, 1H, **H<sup>6'</sup>**); 8.26 (d, 1H, **H<sup>5</sup>**); 8.24 (d, 1H, **H<sup>3'</sup>**); 7.85  
407 (dd, 2H, **ortho H**); 7.72 (td, 1H, **H<sup>4'</sup>**); 7.54 (td, 2H, **meta H**); 7.47 (t, 1H, **para H**); 7.10 (dd, 1H, **H<sup>5'</sup>**);  
408 6.92 (dd, 1H, **H<sup>7</sup>**); 6.65 (td, 1H, **H<sup>6</sup>**).

409 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.71 (d, 1H, **H<sup>8</sup>**); 8.61 (d, 1H, **H<sup>6'</sup>**); 8.30 (d, 1H, **H<sup>3'</sup>**); 8.21 (d, 1H, **H<sup>5</sup>**); 7.85 (d,  
410 2H, **ortho H**); 7.74 (t, 1H, **H<sup>4'</sup>**); 7.58 (t, 2H, **meta H**); 7.49 (t, 1H, **para H**); 7.11 (dd, 1H, **H<sup>5'</sup>**); 6.95  
411 (td, 1H, **H<sup>7</sup>**); 6.61 (dd, 1H, **H<sup>6</sup>**).

412 <sup>1</sup>H NMR, δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO]: 8.74 (d, 1H, **H<sup>8</sup>**); 8.62 (d, 1H, **H<sup>6'</sup>**); 8.50 (d, 1H, **H<sup>5</sup>**); 8.26 (d, 1H, **H<sup>3'</sup>**); 7.94  
413 (d, 2H, **ortho H**); 7.80 (td, 1H, **H<sup>4'</sup>**); 7.60 (t, 2H, **meta H**); 7.51 (t, 1H, **para H**); 7.16 (dd, 1H, **H<sup>5'</sup>**);  
414 7.04 (dd, 1H, **H<sup>7</sup>**); 6.84 (t, 1H, **H<sup>6</sup>**).

415

416 **L<sup>2</sup> (3-(*o*-tolyl)-1-(pyridin-2-yl)imidazo[1,5-*a*]pyridine)**

417 To a solution of bis(2-pyridyl)ketone (0.9209 g; 5.00 mmol) in acetic acid (30 ml) were added *o*-  
418 tolylaldehyde (1.20 ml; 10 mmol) and ammonium acetate (1.9003 g; 25 mmol). The pale yellow  
419 solution was refluxed under inert atmosphere for 5h. The solution was then put in a mixture of

420 water/ice (250 ml), extracted with dichloromethane, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to  
 421 small volume. The product was purified with a chromatographic column using a mixture of ethyl  
 422 acetate and n-hexane (8:2). The solution was concentrated to a small volume and n-hexane was added  
 423 to give a yellow precipitate (**L**<sup>2</sup>). Yield: 0.8560 g (60%).

424 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: 8.71 (d, 1H, **H**<sup>8</sup>); 8.64 (d, 1H, **H**<sup>6'</sup>); 8.23 (d, 1H, **H**<sup>3'</sup>); 7.70 (t, 1H, **H**<sup>4'</sup>); 7.64 (d,  
 425 1H, **H**<sup>5</sup>); 7.51 (d, 1H, **H**<sup>6''</sup>); 7.40 (m, 3H, **H**<sup>5''</sup>+**H**<sup>4''</sup>+**H**<sup>3''</sup>); 7.09 (t, 1H, **H**<sup>5'</sup>); 6.93 (dd, 1H, **H**<sup>7</sup>); 6.60 (t,  
 426 1H, **H**<sup>6</sup>), 2.26 (s, 3H, **CH**<sub>3</sub>).

427 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.71 (d, 1H, **H**<sup>8</sup>); 8.63 (d, 1H, **H**<sup>6'</sup>); 8.20 (d, 1H, **H**<sup>3'</sup>); 7.73 (t, 1H, **H**<sup>4'</sup>); 7.69 (d,  
 428 1H, **H**<sup>5</sup>); 7.51 (d, 1H, **H**<sup>6''</sup>); 7.42 (m, 3H, **H**<sup>5''</sup>+**H**<sup>4''</sup>+**H**<sup>3''</sup>); 7.11 (t, 1H, **H**<sup>5'</sup>); 6.96 (t, 1H, **H**<sup>7</sup>); 6.65 (t,  
 429 1H, **H**<sup>6</sup>), 2.27 (s, 3H, **CH**<sub>3</sub>).

430 <sup>1</sup>H NMR, δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO]: 8.72 (d, 1H, **H**<sup>8</sup>); 8.62 (d, 1H, **H**<sup>6'</sup>); 8.21 (d, 1H, **H**<sup>3'</sup>); 7.85 (d, 1H, **H**<sup>5</sup>); 7.78  
 431 (td, 1H, **H**<sup>4'</sup>); 7.56 (d, 1H, **H**<sup>6''</sup>); 7.44 (m, 3H, **H**<sup>5''</sup>+**H**<sup>4''</sup>+**H**<sup>3''</sup>); 7.15 (dd, 1H, **H**<sup>5'</sup>); 7.03 (dd, 1H, **H**<sup>7</sup>);  
 432 6.78 (t, 1H, **H**<sup>6</sup>), 2.27 (s, 3H, **CH**<sub>3</sub>).

433

#### 434 **L**<sup>3</sup> (3-mesityl-1-(pyridin-2-yl)imidazo[1,5-*a*]pyridine)

435 To a solution of bis(2-pyridyl)ketone (0.9207 g; 5.00 mmol) in acetic acid (30 ml) were added  
 436 mesitylaldehyde (1.04 ml; 10 mmol) and ammonium acetate (1.9023 g; 25 mmol). The pale yellow  
 437 solution was refluxed under inert atmosphere for 5 h. The solution was then put in a mixture of  
 438 water/ice (250 ml), extracted with dichloromethane, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to  
 439 small volume. The product was purified with a chromatographic column using a mixture of ethyl  
 440 acetate and n-hexane (8:2). The solution was concentrated to a small volume and n-hexane was added  
 441 to give a yellow precipitate (**L**<sup>3</sup>). Yield: 0.9088 g (58%).

442 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: 8.94 (d, 1H, **H**<sup>8</sup>); 8.89 (d, 1H, **H**<sup>6'</sup>); 8.48 (d, 1H, **H**<sup>3'</sup>); 7.95 (td, 1H, **H**<sup>4'</sup>); 7.61  
 443 (d, 1H, **H**<sup>5</sup>); 7.33 (dd, 1H, **H**<sup>5'</sup>); 7.26 (s, 2H, *meta* **H**); 7.17 (dd, 1H, **H**<sup>7</sup>); 6.82 (td, 1H, **H**<sup>6</sup>); 2.62 (s,  
 444 3H, *para* **CH**<sub>3</sub>); 2.27 (s, 6H, *ortho* **CH**<sub>3</sub>).

445 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.68 (d, 1H, **H**<sup>8</sup>); 8.62 (d, 1H, **H**<sup>6'</sup>); 8.20 (d, 1H, **H**<sup>3'</sup>); 7.72 (t, 1H, **H**<sup>4'</sup>); 7.36  
 446 (d, 1H, **H**<sup>5</sup>); 7.09 (t, 1H, **H**<sup>5'</sup>); 7.05 (s, 2H, *meta* **H**); 6.93 (t, 1H, **H**<sup>6</sup>); 6.60 (t, 1H, **H**<sup>7</sup>); 2.38 (s, 3H, *para*  
 447 **CH**<sub>3</sub>); 1.99 (s, 3H, *ortho* **CH**<sub>3</sub>).

448 <sup>1</sup>H NMR, δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO]: 8.71 (d, 1H, **H**<sup>8</sup>); 8.62 (d, 1H, **H**<sup>6'</sup>); 8.20 (d, 1H, **H**<sup>3'</sup>); 7.77 (td, 1H, **H**<sup>4'</sup>);  
 449 7.51 (d, 1H, **H**<sup>5</sup>); 7.14 (dd, 1H, **H**<sup>5'</sup>); 7.08 (s, 2H, *meta* **H**); 7.02 (dd, 1H, **H**<sup>7</sup>); 6.75 (t, 1H, **H**<sup>6</sup>); 2.37  
 450 (s, 3H, *para* **CH**<sub>3</sub>); 1.99 (s, 6H, *ortho* **CH**<sub>3</sub>).

451

452

453

454 **L<sup>4</sup> (3-benzyl-1-(pyridin-2-yl)imidazo[1,5-*a*]pyridine)**View Article Online  
DOI: 10.1039/D1DT00546D

455 To a solution of bis(2-pyridyl)ketone (1.3998 g; 7.60 mmol) in methanol (30 ml) were added  
456 phenylalanine (1.2554 g; 7.6 mmol) and slowly few drops of acetic acid. The pale yellow solution  
457 was refluxed in an inert atmosphere for 12 h. The resulting orange solution was concentrated to a  
458 small volume and diethyl ether added to give a product which was purified with a chromatographic  
459 column using a mixture of ethyl acetate and n-hexane (8:2). The solution was evaporated completely  
460 to give **L<sup>4</sup>** as a brown oil. Yield: 1.4963 g (69%).

461 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: 8.62 (d, 1H, **H<sup>6'</sup>**); 8.60 (d, 1H, **H<sup>8</sup>**); 8.17 (d, 1H, **H<sup>3'</sup>**); 7.71 (td, 1H, **H<sup>4'</sup>**); 7.59  
462 (d, 1H, **H<sup>5</sup>**); 7.24 (m, 5H, **H<sup>ar</sup>**); 7.07 (dd, 1H, **H<sup>5'</sup>**); 6.84 (dd, 1H, **H<sup>7</sup>**); 6.52 (t, 1H, **H<sup>6</sup>**); 4.51 (s, 2H,  
463 **CH<sub>2</sub>**).

464 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.62 (d, 1H, **H<sup>8'</sup>**); 8.60 (d, 1H, **H<sup>6'</sup>**); 8.16 (d, 1H, **H<sup>3'</sup>**); 7.73 (t, 1H, **H<sup>4'</sup>**); 7.68  
465 (d, 1H, **H<sup>5</sup>**); 7.27 (m, 5H, **H<sup>ar</sup>**); 7.10 (t, 1H, **H<sup>5'</sup>**); 6.88 (t, 1H, **H<sup>7</sup>**); 6.59 (t, 1H, **H<sup>6</sup>**); 4.49 (s, 2H,  
466 **CH<sub>2</sub>**).

467 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>3</sub>COCD<sub>3</sub>]: 8.62 (d, 1H, **H<sup>8</sup>**); 8.58 (d, 1H, **H<sup>6'</sup>**); 8.20 (d, 1H, **H<sup>3'</sup>**); 8.03 (d, 1H, **H<sup>5</sup>**);  
468 8.02 (t, 1H, **H<sup>4'</sup>**); 7.25 (m, 5H, **H<sup>ar</sup>**); 7.12 (dd, 1H, **H<sup>5'</sup>**); 6.92 (dd, 1H, **H<sup>7</sup>**); 6.69 (t, 1H, **H<sup>6</sup>**); 4.52 (s,  
469 2H, **CH<sub>2</sub>**).

470 <sup>1</sup>H NMR, δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>SO]: 8.56 (d, 1H, **H<sup>6'</sup>**); 8.47 (d, 1H, **H<sup>8</sup>**); 8.16 (d, 1H, **H<sup>5</sup>**); 8.05 (d, 1H, **H<sup>3'</sup>**);  
471 7.78 (t, 1H, **H<sup>4'</sup>**); 7.27 (s, br 5H, **H<sup>ar</sup>**); 7.17 (dd, 1H, **H<sup>5'</sup>**); 6.97 (t, 1H, **H<sup>7</sup>**); 6.75 (t, 1H, **H<sup>6</sup>**); 4.48 (s,  
472 2H, **CH<sub>2</sub>**).

474 **L<sup>1i</sup> (1-phenyl-3-(pyridin-2-yl)imidazo[1,5-*a*] pyridine)**

475 To a solution of 2-benzoylpyridine (0.9160 g; 5 mmol) in toluene (25 ml) were added benzyl  
476 ammine (950 μL; 5.5 mmol), iodide (1.5302 g; 6 mmol) and sodium acetate (1.2302 g; 15  
477 mmol). The dark solution was refluxed in an inert atmosphere for 6 h, until to disappear of the  
478 ketone. At the solution was added Na<sub>2</sub>SO<sub>3</sub> (5%) and the mixture was extracted with dichloro  
479 methane and water. The organic fraction was anhydriified with Na<sub>2</sub>SO<sub>4</sub> and filtered. The product  
480 was purified with a chromatographic column using a mixture of ethyl acetate and petroleum  
481 ether (1:3) and obtained as a yellow precipitate (**L<sup>1i</sup>**). Yield: 0.5964 g (44%).

482 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: 10.03 (d, 1H, **H<sup>5</sup>**); 8.65 (d, 1H, **H<sup>6'</sup>**); 8.49 (d, 1H, **H<sup>3'</sup>**); 7.97 (d, 2H, **ortho**  
483 **H**); 7.90 (d, 1H, **H<sup>8</sup>**); 7.79 (td, 1H, **H<sup>4'</sup>**); 7.49 (t, 2H, **meta H**); 7.32 (t, 1H, **para H**); 7.21 (dd,  
484 1H, **H<sup>5'</sup>**); 6.94 (dd, 1H, **H<sup>7</sup>**); 6.77 (t, 1H, **H<sup>6</sup>**).

485 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>3</sub>COCD<sub>3</sub>]: 10.08 (d, 1H, **H<sup>5</sup>**); 8.695 (d, 1H, **H<sup>6'</sup>**); 8.48 (d, 1H, **H<sup>8</sup>**); 8.04 (m, 3H,  
486 **ortho H+H<sup>3'</sup>**); 7.93 (td, 1H, **H<sup>4'</sup>**); 7.49 (t, 2H, **meta H**); 7.33 (t, 1H, **para H+H<sup>5'</sup>**); 7.07 (t, 1H, **H<sup>6</sup>**);  
487 6.91 (t, 1H, **H<sup>7</sup>**).

488 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>3</sub>)<sub>2</sub>SO]: 9.97 (d, 1H, **H**<sup>5</sup>); 8.715 (d, 1H, **H**<sup>6</sup>); 8.10 (d, 1H, **H**<sup>8</sup>); 8.04 (m, 3H, **ortho**  
 489 **H**+**H**<sup>3'</sup>); 7.51 (t, 2H, **H**<sup>ar</sup>); 7.39 (t, 1H, **H**<sup>4</sup>); 7.33 (t, 1H, **H**<sup>5</sup>); 7.11 (t, 1H, **H**<sup>6</sup>); 6.99 (t, 1H, **H**<sup>7</sup>).

490

491

492 *Synthesis of the complexes*493 **[Pd(L<sup>1</sup>)Cl<sub>2</sub>] (1-Cl)**

494 To a solution of **L**<sup>1</sup> (0.1193 g; 0.44 mmol) in acetic acid (25 ml) was added Pd(OAc)<sub>2</sub> (0.0988 g; 0.44  
 495 mmol). The orange solution was refluxed under inert atmosphere for 6 h and evaporated to dryness.  
 496 The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for  
 497 12 h at room temperature then filtered. The resulting solution was concentrated to a small volume and  
 498 diethyl ether added to give a precipitate which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the  
 499 analytical sample as yellow solid (**1-Cl**). Yield: 0.0947 g (48%). M.p.: 276 °C

500 Found: C **47.85**; H **2.80**; N **9.25** %. Calc. for C<sub>18</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>3</sub>Pd: C, 48.19; H, 2.92; N, 9.37.

501 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.10 (d, 1H, **H**<sup>6'</sup>); 7.98 (d, 1H, **H**<sup>3'</sup>); 7.97 (t, 2H, **H**<sup>5</sup>); 7.91 (d, 1H, **H**<sup>8</sup>); 7.85  
 502 (t, 1H, **H**<sup>4</sup>); 7.65 (m, 5H, **H**<sup>ar</sup>); 7.33 (d, 1H, **H**<sup>7</sup>); 7.22 (t, 1H, **H**<sup>5</sup>); 6.89 (t, 1H, **H**<sup>6</sup>).

503

504 **[Pd(L<sup>2</sup>)Cl<sub>2</sub>] (2-Cl)**

505 To a solution of **L**<sup>2</sup> (0.1259 g; 0.44 mmol) in acetic acid (25 ml) was added Pd(OAc)<sub>2</sub> (0.0987 g; 0.44  
 506 mmol). The orange solution was refluxed under inert atmosphere for 6 h and evaporated to dryness.  
 507 The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for  
 508 12 h at room temperature then filtered. The resulting solution was concentrated to a small volume and  
 509 diethyl ether added to give a precipitate which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the  
 510 analytical sample as yellow solid (**2-Cl**). Yield: 0.0997 g (49%). M.p.: 215 °C

511 Found: C **49.30**; H **2.99**; N **8.94**%. Calc. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>Pd: C, 49.32; H, 3.27; N, 9.08.

512 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.25 (d, 1H, **H**<sup>6'</sup>); 8.03 (t, 1H, **H**<sup>4</sup>); 7.95 (d, 1H, **H**<sup>8</sup>); 7.85 (d, 1H, **H**<sup>3'</sup>); 7.55  
 513 (m, 2H, **H**<sup>6''</sup>+**H**<sup>5</sup>); 7.41 (m, 5H, **H**<sup>5''</sup>+**H**<sup>4''</sup>+ **H**<sup>3''</sup>+**H**<sup>5'</sup>+ **H**<sup>7</sup>); 6.88 (t, 1H, **H**<sup>6</sup>); 2.21 (s, 3H, **CH**<sub>3</sub>).

514

515

516 **[Pd(L<sup>3</sup>)Cl<sub>2</sub>] (3-Cl)**

517 To a solution of **L**<sup>3</sup> (0.1391 g; 0.44 mmol) in acetic acid (25 ml) was added Pd(OAc)<sub>2</sub> (0.0988 g; 0.44  
 518 mmol). The orange solution was refluxed under inert atmosphere for 6 h and evaporated to dryness.  
 519 The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for  
 520 12h at room temperature then filtered. The resulting solution was concentrated to a small volume and

521 diethyl ether added to give a precipitate which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the  
522 analytical sample as yellow solid (**3-Cl**). Yield: 0.1900 g (88%). M.p.: > 290 °C  
523 Found: C **51.04**; H **3.50**; N **8.46**%. Calc. for C<sub>21</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>3</sub>Pd: C, 51.40; H, 3.90; N, 8.56.  
524 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.26 (d, 1H, **H<sup>6'</sup>**); 8.01 (t, 1H, **H<sup>4'</sup>**); 7.93 (d, 1H, **H<sup>8</sup>**); 7.84 (d, 1H, **H<sup>5</sup>**); 7.43  
525 (d, 1H, **H<sup>3'</sup>**); 7.33 (m, 2H, **H<sup>5'</sup>+H<sup>7</sup>**); 7.08 (s, 2H, *meta* **H**); 6.87 (t, 1H, **H<sup>6</sup>**); 2.41 (s, 3H, *para* **CH<sub>3</sub>**);  
526 2.03 (s, 6H, *ortho* **CH<sub>3</sub>**).

#### 527 528 **[Pd(L<sup>4</sup>)Cl<sub>2</sub>] (4-Cl)**

529 To a solution of **L<sup>4</sup>** (0.1251 g; 0.44 mmol) in acetic acid (50 ml) was added Pd(OAc)<sub>2</sub> (0.0989 g; 0.44  
530 mmol). The solution was refluxed under inert atmosphere for 6 h and evaporated to dryness. The  
531 crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for 12 h  
532 at room temperature then filtered. The resulting solution was concentrated to a small volume and diethyl  
533 ether added to give a precipitate which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical  
534 sample as yellow solid (**4-Cl**). Yield: 0.0631 g (31%). M.p.: 225 °C

535 Found: C **49.30**; H **2.99**; N **8.90**%. Calc. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>Pd: C, 49.32; H, 3.27; N, 9.08.

536 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.27 (d, 1H, **H<sup>6'</sup>**); 7.97 (t, 1H, **H<sup>4'</sup>**); 7.89 (m, 2H, **H<sup>8</sup>+H<sup>3'</sup>**); 7.77 (d, 1H, **H<sup>5</sup>**);  
537 7.34 (m, 5H, **H<sup>ar</sup>**); 7.27 (m, 2H, **H<sup>5'</sup>+H<sup>7</sup>**); 6.88 (t, 1H, **H<sup>6</sup>**); 4.44 (broad, 2H, **CH<sub>2</sub>**).

#### 538 539 **[Pd(L<sup>1</sup>)(OAc)<sub>2</sub>] (1-OAc)**

540 To a solution of **L<sup>1</sup>** (0.1193 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)<sub>2</sub> (0.0988  
541 g; 0.44 mmol). The orange solution was stirred for 12 h at room temperature, then evaporated to a  
542 small volume and diethyl ether added. The yellow precipitate formed was filtered off and  
543 recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid (**1-OAc**). Yield:  
544 0.2050 g (94%). M.p.: 176 °C

545 Found: C **52.95**; H **3.74**; N **8.30**%. Calc. for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>Pd: C, 53.29; H, 3.86; N, 8.47.

546 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.12 (d, 1H, **H<sup>6'</sup>**); 7.98 (td, 1H, **H<sup>4'</sup>**); 7.91 (d, 1H, **H<sup>8</sup>**); 7.85 (d, 1H, **H<sup>5</sup>**); 7.80  
547 (d, 1H, **H<sup>3'</sup>**); 7.67-7.60 (m, 5H, **H<sup>ar</sup>**); 7.29 (dd, 1H, **H<sup>7</sup>**); 7.24 (t, 1H, **H<sup>5'</sup>**); 6.86 (t, 1H, **H<sup>6</sup>**); 1.99 (s,  
548 3H, C(O)**CH<sub>3</sub>**); 1.13 (s, 3H, C(O)**CH<sub>3</sub>**).

#### 549 550 **[Pd(L<sup>2</sup>)(OAc)<sub>2</sub>] (2-OAc)**

551 To a solution of **L<sup>2</sup>** (0.1259 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)<sub>2</sub> (0.0987  
552 g; 0.44 mmol). The orange solution was stirred for 12 h at room temperature, then evaporated to a  
553 small volume and diethyl ether added. The yellow-green precipitate was filtered off and recrystallized

554 from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as yellow solid (**2-OAc**). Yield: 0.0919 g (41%).

555 M.p.: 250 °C

556 Found: C **53.90**; H **3.95**; N **7.99** %. Calc. for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Pd: C, 54.18; H, 4.15; N, 8.24.

557 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.14 (d, 1H, **H<sup>6'</sup>**); 7.98 (d, 1H, **H<sup>4'</sup>**); 7.89 (d, 1H, **H<sup>8</sup>**); 7.79 (d, 1H, **H<sup>5</sup>**); 7.51  
558 (d, 1H, **H<sup>3'</sup>**); 7.50-7.40 (m, 4H, **H<sup>ar</sup>**); 7.31 (t, 1H, **H<sup>7</sup>**); 7.25 (t, 1H, **H<sup>5'</sup>**); 6.86 (t, 1H, **H<sup>6</sup>**); 2.26 (s, 3H,  
559 *ortho* CH<sub>3</sub>); 1.98 (s, 3H, C(O)CH<sub>3</sub>); 1.11 (s, 3H, C(O)CH<sub>3</sub>).

560

### 561 [Pd(L<sup>3</sup>)(OAc)<sub>2</sub>] (**3-OAc**)

562 To a solution of L<sup>3</sup> (0.1383 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)<sub>2</sub> (0.0985  
563 g; 0.44 mmol). The orange solution was stirred for 12 h at room temperature, then evaporated to a  
564 small volume and diethyl ether added. The yellow precipitate formed was filtered off and  
565 recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid (**3-OAc**). Yield:  
566 0.2130 g (90%). M.p.: 268 °C

567 Found: C **55.01**; H **4.15**; N **7.64**%. Calc. for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>Pd: C, 55.82; H, 4.68; N, 7.81.

568 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.14 (d, 1H, **H<sup>6'</sup>**); 7.98 (t, 1H, **H<sup>4'</sup>**); 7.89 (d, 1H, **H<sup>8</sup>**); 7.77 (d, 1H, **H<sup>5</sup>**); 7.40  
569 (d, 1H, **H<sup>3'</sup>**); 7.30 (t, 1H, **H<sup>5'</sup>**); 7.24 (t, 1H, **H<sup>7</sup>**); 7.04 (s, 2H, *meta* H); 6.85 (t, 1H, **H<sup>6</sup>**); 2.35 (s, 3H,  
570 *para* CH<sub>3</sub>); 2.09 (s, 6H, *ortho* CH<sub>3</sub>); 1.98 (s, 3H, C(O)CH<sub>3</sub>); 1.13 (s, 3H, C(O)CH<sub>3</sub>).

571

### 572 [Pd(L<sup>4</sup>)(OAc)<sub>2</sub>] (**4-OAc**)

573 To a solution of L<sup>4</sup> (0.1259 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)<sub>2</sub> (0.0986  
574 g; 0.44 mmol). The orange solution was stirred for 12 h at room temperature, then evaporated to a  
575 small volume and diethyl ether added. The yellow precipitate formed was filtered off and  
576 recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid (**4-OAc**). Yield:  
577 0.1435 g (64%). M.p.: 260 °C

578 Found: C **53.90**; H **3.94**; N **8.02**%. Calc. for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Pd: C, 54.18; H, 4.15; N, 8.24.

579 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 8.07 (d, 1H, **H<sup>6'</sup>**); 7.92 (t, 1H, **H<sup>4'</sup>**); 7.84 (t, 2H, **H<sup>5</sup>+H<sup>8</sup>**); 7.74 (d, 1H, **H<sup>3'</sup>**);  
580 7.35-7.23 (m, 5H, **H<sup>ar</sup>**); 7.16 (m, 2H, **H<sup>5'</sup>+H<sup>7</sup>**); 6.77 (t, 1H, **H<sup>6</sup>**); 4.61 (s, 2H, CH<sub>2</sub>); 2.10 (s, 3H, Pd-  
581 CH<sub>3</sub>); 1.73 (s, 3H, Pd-CH<sub>3</sub>).

582

### 583 [Pt(L<sup>1</sup>)Cl<sub>2</sub>] (**5**)

584 To a solution of K<sub>2</sub>PtCl<sub>4</sub> (0.1005 g; 0.24 mmol) in H<sub>2</sub>O (25 ml) were added L<sup>1</sup> (0.0651 g; 0.24 mmol)  
585 and slowly few drops of HCl (2 M). The mixture was heated at reflux under inert atmosphere for 72  
586 h, until the solution was colourless, and then cooled. The yellow precipitate was filtered off, washed

587 with water, ethanol and diethyl ether and finally recrystallised from dichloromethane and diethyl ether  
 588 to give the analytical sample as a yellow solid (**5**). Yield: 0.1225 g (95%). M.p.: > 290 °C  
 589 Found: C **39.97**; H **2.10**; N **7.63**%. Calc. for C<sub>18</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>3</sub>Pt: C, 40.24; H, 2.44; N, 7.82.

590 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>] : 9.51 (d, 1H, <sup>3</sup>J<sub>Pt-H</sub>= 36 Hz, **H<sup>6'</sup>**); 8.05 (t, 1H, **H<sup>4'</sup>**); 7.95 (d, 1H, **H<sup>8</sup>**); 7.84 (m,  
 591 2H, **H<sup>3'</sup>+H<sup>5</sup>**); 7.66 (m, 5H, **H<sup>ar</sup>**); 7.33 (m, 2H, **H<sup>5'</sup>+H<sup>7</sup>**); 6.92 (t, 1H, **H<sup>6</sup>**).

592

### 593 [Pt(L<sup>2</sup>)Cl<sub>2</sub>] (**6**)

594 To a solution of K<sub>2</sub>PtCl<sub>4</sub> (0.1001 g; 0.24 mmol) in H<sub>2</sub>O (25 ml) were added L<sup>2</sup> (0.0687 g; 0.24 mmol)  
 595 and slowly few drops of HCl (2 M). The mixture was heated at reflux under inert atmosphere for 72  
 596 h, until the solution was colourless, and then cooled. The yellow precipitate was filtered off, washed  
 597 with water, ethanol and diethyl ether and finally recrystallised from dichloromethane and diethyl ether  
 598 to give the analytical sample as a yellow solid (**6**). Yield: 0.0793 g (60%). M.p.: > 290 °C  
 599 Found: C **41.01**; H **2.53**; N **7.44**%. Calc. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>Pt: C, 41.39; H, 2.74; N, 7.62.

600 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.63 (d, 1H, <sup>3</sup>J<sub>Pt-H</sub>= 34Hz, **H<sup>6'</sup>**); 8.07 (t, 1H, **H<sup>4'</sup>**); 7.96 (d, 1H, **H<sup>8</sup>**); 7.86 (d,  
 601 1H, **H<sup>3'</sup>**); 7.62-7.28 (m, 7H, **H<sup>5</sup>+ H<sup>Ar</sup>+H<sup>5'</sup>+H<sup>7</sup>**); 6.91 (t, 1H, **H<sup>6</sup>**); 2.22 (s, 3H, **CH<sub>3</sub>**).

602

### 603 [Pt(L<sup>3</sup>)Cl<sub>2</sub>] (**7**)

604 To a solution of K<sub>2</sub>PtCl<sub>4</sub> (0.1002 g; 0.24 mmol) in H<sub>2</sub>O (25 ml) were added L<sup>3</sup> (0.0754 g; 0.24 mmol)  
 605 and slowly few drops of HCl (2 M). The mixture was heated at reflux under inert atmosphere for 72  
 606 h, until the solution was colourless, and then cooled. The yellow precipitate was filtered off, washed  
 607 with water, ethanol and diethyl ether and finally recrystallised from dichloromethane and diethyl ether  
 608 to give the analytical sample as a yellow solid (**7**). Yield: 0.0750 g (54%). M.p.: > 290 °C  
 609 Found: C **43.10**; H **2.97**; N **7.03**%. Calc. for C<sub>21</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>3</sub>Pt: C, 43.53; H, 3.31; N, 7.25.

610 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.63 (d, 1H, <sup>3</sup>J<sub>Pt-H</sub>= 37 Hz, **H<sup>6'</sup>**); 8.07 (t, 1H, **H<sup>4'</sup>**); 7.97 (d, 1H, **H<sup>8</sup>**); 7.87 (d,  
 611 1H, **H<sup>3'</sup>**); 7.43 (d, 1H, **H<sup>5</sup>**); 7.37 (t, H, **H<sup>7</sup>**); 7.31 (t, H, **H<sup>5'</sup>**); 7.07 (s, 2H, *meta* **H<sup>Ar</sup>**); 6.91 (t, 1H, **H<sup>6</sup>**);  
 612 2.42 (s, 3H, *para* **CH<sub>3</sub>**); 2.03 (s, 6H, *ortho* **CH<sub>3</sub>**).

613

### 614 [Pt(L<sup>4</sup>)Cl<sub>2</sub>] (**8**)

615 To a solution of K<sub>2</sub>PtCl<sub>4</sub> (0.1003 g; 0.24 mmol) in H<sub>2</sub>O (25 ml) were added L<sup>4</sup> (0.0687 g; 0.24 mmol)  
 616 and slowly few drops of HCl (2 M). The mixture was heated at reflux under inert atmosphere for 72  
 617 h, until the solution was colourless, and then cooled. The yellow precipitate was filtered off, washed  
 618 with water, ethanol and diethyl ether and finally recrystallised from dichloromethane and diethyl ether  
 619 to give the analytical sample as a yellow solid (**8**). Yield: 0.0436g (33%). M.p.: > 290 °C

620 Found: C **40.97**; H **2.36**; N **7.51**%. Calc. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>Pt: C, 41.39; H, 2.74; N, 7.62. View Article Online  
DOI: 10.1039/D1DT00546D  
 621 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: 9.65 (d, 1H, <sup>3</sup>J<sub>Pt-H</sub>= 38.0 Hz, **H<sup>6'</sup>**); 8.02 (t, 1H, **H<sup>4'</sup>**); 7.90 (t, 2H, **H<sup>8</sup>+H<sup>3'</sup>**); 7.79  
 622 (d, 1H, **H<sup>5'</sup>**); 7.38-7.21 (m, 7H, **H<sup>5'</sup>+H<sup>7</sup>+H<sup>ar</sup>**); 6.91 (t, 1H, **H<sup>6'</sup>**); 5.41 (s, 2H, **CH<sub>2</sub>**).

623 <sup>1</sup>H NMR, δ<sub>H</sub>[DMSO-d<sub>6</sub>]: 9.39 (d, br 1H, **H<sup>6'</sup>**); 8.33 (m, 2H, **H<sup>8</sup>+H<sup>5'</sup>**); 8.22 (m, 2H, **H<sup>3'</sup>+H<sup>4'</sup>**); 7.51-  
 624 7.22 (m, 8H, **H<sup>5'</sup>+H<sup>7</sup>+H<sup>ar</sup>**); 7.12 (t, 1H, **H<sup>6'</sup>**); 5.41 (s, 2H, **CH<sub>2</sub>**).

625

### 626 [Pd(L<sup>1</sup>)(CH<sub>3</sub>)Cl] (**9**)

627 To a solution of L<sup>1</sup> (0.0976 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous  
 628 stirring [Pd(COD)(CH<sub>3</sub>)(Cl)] (0.0954 g; 0.36 mmol). The yellow solution was stirred for 24 h at room  
 629 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
 630 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
 631 yellow solid (**9**). Yield: 0.1341 g (87%).

632 Found: C **54.02**; H **4.01**; N **9.73**%. Calc. for C<sub>19</sub>H<sub>16</sub>ClN<sub>3</sub>Pd: C, 53.29; H, 3.77; N, 9.81.

633 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: *Major geometric isomer*: 9.11 (d, 1H, **H<sup>6'</sup>**); 7.94 (d, 1H, **H<sup>8</sup>**); 7.86-7.79 (m, 3H,  
 634 **H<sup>3'</sup>+H<sup>4'</sup>+H<sup>5'</sup>**); 7.64-7.53 (m, 5H, **H<sup>ar</sup>**); 7.24 (td, 1H, **H<sup>5'</sup>**); 7.18 (dd, 1H, **H<sup>7</sup>**); 6.78 (t, 1H, **H<sup>6'</sup>**); 0.35 (s,  
 635 3H, Pd-**CH<sub>3</sub>**)

636 *minor geometric isomer*: 8.51 (d, 1H, **H<sup>6'</sup>**); 7.71 (m, 5H, **H<sup>ar</sup>**); 6.86 (t, 1H, **H<sup>6'</sup>**); 1.04 (s, 3H, Pd-**CH<sub>3</sub>**).

637

### 638 [Pd(L<sup>2</sup>)(CH<sub>3</sub>)Cl] (**10**)

639 To a solution of L<sup>2</sup> (0.1030 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous  
 640 stirring [Pd(COD)(CH<sub>3</sub>)(Cl)] (0.0955 g; 0.36 mmol). The yellow solution was stirred for 24 h at room  
 641 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
 642 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
 643 yellow solid (**10**). Yield: 0.1353 g (85%).

644 Found: C **54.95**; H **4.61**; N **9.27**%. Calc. for C<sub>20</sub>H<sub>18</sub>ClN<sub>3</sub>Pd: C, 54.32; H, 4.10; N, 9.50.

645 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: *Major geometric isomer*: 9.13 (d, 1H, **H<sup>6'</sup>**); 7.95 (d, 1H, **H<sup>8</sup>**); 7.85 (m, 2H,  
 646 **H<sup>3'</sup>+H<sup>4'</sup>**); 7.52 (t, 1H, **H<sup>5'</sup>**); 7.49 (d, 1H, **H<sup>5'</sup>**); 7.41-7.34 (m 3H **H<sup>ar</sup>**); 7.25(7, 1H, **H<sup>5'</sup>**); 7.19 (dd, 1H,  
 647 **H<sup>7</sup>**); 6.78 (t, 1H, **H<sup>6'</sup>**); 2.41 (s, 3H, **para CH<sub>3</sub>**); 2.02 (s, 6H, **ortho CH<sub>3</sub>**); 0.39 (s, 3H, Pd-**CH<sub>3</sub>**).

648 2.15 (s, 1H, **ortho CH<sub>3</sub>**); 0.32 (s, 1H, **CH<sub>3</sub>**)

649 *minor geometric isomer*: 8.51 (d, 1H, **H<sup>6'</sup>**), 2.25 (s, 1H, **ortho CH<sub>3</sub>**); 1.00 (s, 1H, Pd-**CH<sub>3</sub>**).

650

### 651 [Pd(L<sup>3</sup>)(CH<sub>3</sub>)Cl] (**11**)

652 To a solution of L<sup>3</sup> (0.1131 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous  
 653 stirring [Pd(COD)(CH<sub>3</sub>)(Cl)] (0.0953 g; 0.36 mmol). The yellow solution was stirred for 24 h at room

654 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
 655 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
 656 yellow solid (**11**). Yield: 0.1286 g (76%).

657 Found: C **56.99**; H **4.97**; N **8.70**%. Calc. for C<sub>22</sub>H<sub>22</sub>ClN<sub>3</sub>Pd: C, 56.18; H, 4.72; N, 8.93.

658 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: *Major geometric isomer*: 9.18 (d, 1H, **H<sup>6'</sup>**); 7.96 (d, 1H, **H<sup>8</sup>**); 7.88 (m, 2H,  
 659 **H<sup>3'</sup>+H<sup>4'</sup>**); 7.41 (d, 1H, **H<sup>5</sup>**); 7.30 (t, 1H, **H<sup>5'</sup>**); 7.22 (t, 1H, **H<sup>7</sup>**); 7.04 (s, 2H, **meta H**); 6.79 (t, 1H, **H<sup>6</sup>**);  
 660 2.41 (s, 3H, **para CH<sub>3</sub>**); 2.02 (s, 6H, **ortho CH<sub>3</sub>**); 0.39 (s, 3H, **Pd-CH<sub>3</sub>**).

661 *minor geometric isomer*: 8.55 (d, 1H, **H<sup>6'</sup>**); 6.99 (s, 2H, **meta H**); 6.86 (t, 1H, **H<sup>6</sup>**); 2.38 (s, 3H, **para**  
 662 **CH<sub>3</sub>**); 2.03 (s, 6H, **ortho CH<sub>3</sub>**); 1.01 (s, 3H, **Pd-CH<sub>3</sub>**).

663

#### 664 [Pd(L<sup>4</sup>)(CH<sub>3</sub>)Cl] (**12**)

665 To a solution of L<sup>4</sup> (0.1255 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous  
 666 stirring [Pd(COD)(CH<sub>3</sub>)Cl] (0.0957 g; 0.36 mmol). The yellow solution was stirred for 24 h at room  
 667 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
 668 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
 669 yellow solid (**12**). Yield: 0.0429 g (27%).

670 Found: C **54.95**; H **4.69**; N **9.29**%. Calc. for C<sub>20</sub>H<sub>18</sub>ClN<sub>3</sub>Pd: C, 54.32; H, 4.10; N, 9.50.

671 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>]: *Major geometric isomer*: 8.56 (d, 1H, **H<sup>6'</sup>**); 7.89-7.80 (m, 4H, **H<sup>8</sup> H<sup>3'</sup>+H<sup>4'</sup>+H<sup>5</sup>**);  
 672 7.41-7.26 (m, 5H, **H<sup>ar</sup>**); 7.21 (t, 1H, **H<sup>7</sup>**); 7.12 (dd, 1H, **H<sup>5'</sup>**); 6.74 (t, 1H, **H<sup>6</sup>**); 5.15 (s, 2H, **CH<sub>2</sub>**); 1.17  
 673 (s, 3H, **Pd-CH<sub>3</sub>**).

674 *minor geometric isomer*: 9.23 (d, 1H, **H<sup>6'</sup>**); 6.75 (s, 1H, **H<sup>6</sup>**); 5.36 (s, 2H, **CH<sub>2</sub>**); 1.26 (s, 3H, **Pd-**  
 675 **CH<sub>3</sub>**).

676

#### 677 [Pt(L<sup>1</sup>)(CH<sub>3</sub>)Cl] (**13**)

678 To a solution of L<sup>1</sup> (0.0379 g; 0.14 mmol) in dichloromethane (25 ml) was added under vigorous  
 679 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)Cl] (0.0563 g; 0.14 mmol). The yellow solution was stirred for 72 h at room  
 680 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
 681 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
 682 yellow solid (**13**). Yield: 0.0528 g (73 %).

683 Found: C **45.06**; H **3.83**; N **7.95**%. Calc. for C<sub>19</sub>H<sub>16</sub>ClN<sub>3</sub>Pt: C, 44.15; H, 3.12; N, 8.13.

684 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>] *Major geometric isomer*: 9.49 (d, <sup>3</sup>J<sub>Pt-H</sub> not resolved, 1H, **H<sup>6'</sup>**); 8.00-7.91 ( m,  
 685 2H, **H<sup>8</sup>+H<sup>4'</sup>**); 7.85 (d, 1H, **H<sup>5</sup>**); 7.75 (d, 1H, **H<sup>3'</sup>**); 7.65-7.54 ( m, 5H, **H<sup>ar</sup>**); 7.30 (t, 1H, **H<sup>5'</sup>**); 7.22 (dd,  
 686 1H, **H<sup>7</sup>**); 6.82 (t, 1H, **H<sup>6</sup>**); 0.51 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub>= 78.1 Hz, **Pt-CH<sub>3</sub>**); *minor geometric isomer*: 8.96 (d,  
 687 <sup>3</sup>J<sub>Pt-H</sub>= 65.5 Hz 1H, **H<sup>6'</sup>**); 1.09 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub>= 80.4 Hz, **Pt-CH<sub>3</sub>**).

688 **[Pt(L<sup>2</sup>)(CH<sub>3</sub>)Cl] (14)**

689 To a solution of L<sup>2</sup> (0.0400 g; 0.14 mmol) in dichloromethane (25 ml) was added under vigorous  
690 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)Cl] (0.0562 g; 0.14 mmol). The yellow solution was stirred for 72 h at room  
691 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
692 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
693 yellow solid (14). Yield: 0.0661 g (89%).

694 Found: C **46.21**; H **3.87**; N **7.68**%. Calc. for C<sub>20</sub>H<sub>18</sub>ClN<sub>3</sub>Pt: C, 45.25; H, 3.42; N, 7.91.

695 <sup>1</sup>H NMR, δ<sub>H</sub>[CDCl<sub>3</sub>] *Major geometric isomer*: 9.50 (d, <sup>3</sup>J<sub>Pt-H</sub> not resolved, 1H, **H<sup>6</sup>**); 7.99-7.92 (m,  
696 2H, **H<sup>8</sup>+H<sup>4</sup>**); 7.87 (d, 1H, **H<sup>5</sup>**); 7.45 (d, 1H, **H<sup>3</sup>**); 7.42-7.34 (m, 4H, **H<sup>ar</sup>**); 7.30 (t, 1H, **H<sup>5</sup>**); 7.22 (dd,  
697 1H, **H<sup>7</sup>**); 6.81 (t, 1H, **H<sup>6</sup>**); 2.15 (s, 3H, **CH<sub>3</sub>**); 0.51 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub>= 78.1 Hz, **Pt-CH<sub>3</sub>**); *minor geometric*  
698 *isomer*: 8.96 (d, <sup>3</sup>J<sub>Pt-H</sub>= 65.5 Hz 1H, **H<sup>6</sup>**); 2.23 (s, 3H, **CH<sub>3</sub>**); 1.07 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub>= 78.8 Hz, **Pt-CH<sub>3</sub>**).

699

700 **[Pt(L<sup>3</sup>)(CH<sub>3</sub>)Cl] (15)**

701 To a solution of L<sup>3</sup> (0.0377 g; 0.12 mmol) in dichloromethane (25 ml) was added under vigorous  
702 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)Cl] (0.0482 g; 0.12 mmol). The yellow solution was stirred for 72 h at room  
703 temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed  
704 was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a  
705 yellow solid (15). Yield: 0.0603 g (90%).

706 Found: C **48.16**; H **4.29**; N **7.31**%. Calc. for C<sub>22</sub>H<sub>22</sub>ClN<sub>3</sub>Pt: C, 47.27; H, 3.97; N, 7.52.

707 <sup>1</sup>H NMR, δ<sub>H</sub>[CD<sub>2</sub>Cl<sub>2</sub>]: *Major geometric isomer*: 9.43 (d, 1H, **H<sup>6</sup>**); *minor geometric isomer* 8.71 (d,  
708 1H, **H<sup>6</sup>**); 8.12-7.89 (m, 6H); 7.50-7.21 (m, 6H); 7.08 (s, 4H, **meta H**); 6.84 (s, 2H, **H<sup>6</sup>**); 2.41 (*min.*  
709 *st.*, s, 6H, **orto CH<sub>3</sub>**); 2.20 (*min. st.*, s, 3H, **para CH<sub>3</sub>**); 2.02 (*Maj. st.*, s, 6H, **orto CH<sub>3</sub>**); 1.93 (*Maj.*  
710 *st.*, s, 3H, **para CH<sub>3</sub>**); 1.15 (*min. st.*, s, 3H, <sup>2</sup>J<sub>Pt-H</sub>= 71.2 Hz, **Pt-CH<sub>3</sub>**); 0.53 (*Maj. st.*, s, 3H, <sup>2</sup>J<sub>Pt-H</sub>=71.4  
711 Hz, **Pt-CH<sub>3</sub>**).

712

713 **[Pt(L<sup>4</sup>)(CH<sub>3</sub>)Cl] (16)**

714 To a solution of L<sup>4</sup> (0.0715 g; 0.25 mmol) in dichloromethane (25 ml) was added under vigorous  
715 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)Cl] (0.1005 g; 0.25 mmol). The yellow solution was stirred for 72 h at  
716 room temperature then concentrated to small volume and treated with diethyl ether The precipitate  
717 formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample  
718 as a yellow solid (16). Yield: 0.0305 g (23 %). M.p. > 290 °C

719 Found: C **46.17**; H **4.01**; N **7.72**%. Calc. for C<sub>20</sub>H<sub>18</sub>ClN<sub>3</sub>Pt: C, 45.25; H, 3.42; N, 7.91.

720  $^1\text{H NMR}$ ,  $\delta_{\text{H}}[\text{CDCl}_3]$ : 9.04 (d,  $^3J_{\text{Pt-H}} = 60.0$  Hz, 1H,  $\text{H}^6$ ); 7.96 t, 1H,  $\text{H}^4$ ); 7.90-7.84 (m, 2H,  $\text{H}^8 + \text{H}^5$ );  
721 7.76 (d, 1H,  $\text{H}^3$ ); 7.44-7.24 (m, 5H,  $\text{H}^{\text{ar}}$ ); 7.23-7.13 (m, 1H,  $\text{H}^5 + \text{H}^7$ ); 6.81 (t, 1H,  $\text{H}^6$ ); 5.30 (s, 2H,  
722  $\text{CH}_2$ ); 1.24 (s, 3H,  $^2J_{\text{Pt-H}} = 80.1$  Hz,  $\text{Pt-CH}_3$ ).

723

724 **[Pt(L<sup>1</sup>)(CH<sub>3</sub>)<sub>2</sub>] (17)**

725 To a solution of **L<sup>1</sup>** (0.0732 g; 0.27 mmol) in dichloromethane (25 ml) was added under vigorous  
726 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>] (0.1030 g; 0.27 mmol). The yellow solution was stirred for 72 h at room  
727 temperature then concentrated to a small volume and treated with diethyl ether. The precipitate  
728 formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample  
729 as a pale green solid (**17**). Yield: 0.0616 g (46 %). M.p.: 250 °C

730 Found: C **49.03**; H **4.04**; N **8.29**%. Calc. for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>Pt: C, 48.38; H, 3.86; N, 8.46.

731  $^1\text{H NMR}$ ,  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$ : 9.04 (d, 1H,  $^3J_{\text{Pt-H}} = 28.1$  Hz,  $\text{H}^6$ ); 8.29 (d, 1H,  $\text{H}^8$ ); 8.19 (t, 1H,  $\text{H}^4$ ); 8.14  
732 (d, 1H,  $\text{H}^3$ ); 8.06 (d, 1H,  $\text{H}^5$ ); 7.77-7.60 (m, 5H,  $\text{H}^{\text{ar}}$ ); 7.34 (t, 2H,  $\text{H}^5 + \text{H}^7$ ); 7.00 (t, 1H,  $\text{H}^6$ ); 0.76 (s,  
733 3H,  $^2J_{\text{Pt-H}} = 90.0$  Hz,  $\text{Pt-CH}_3$ ); 0.26 (s, 3H,  $^2J_{\text{Pt-H}} = 89.4$  Hz,  $\text{Pt-CH}_3$ ).

734

735 **[Pt(L<sup>2</sup>)(CH<sub>3</sub>)<sub>2</sub>] (18)**

736 To a solution of **L<sup>2</sup>** (0.0744 g; 0.26 mmol) in dichloromethane (25 ml) was added under vigorous  
737 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>] (0.0992 g; 0.26 mmol). The yellow solution was stirred for 72 h at room  
738 temperature then concentrated to a small volume and treated with diethyl ether. The precipitate  
739 formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample  
740 as a pale green solid (**18**). Yield: 0.1194 g (90%). M.p.: 219 °C

741 Found: C **50.05**; H **4.51**; N **8.02**%. Calc. for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>Pt: C, 49.41; H, 4.15; N, 8.23.

742  $^1\text{H NMR}$ ,  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$ : 9.03 (d, 1H,  $^3J_{\text{Pt-H}} = 28.1$  Hz,  $\text{H}^6$ ); 8.31 (d, 1H,  $\text{H}^8$ ); 8.20 (t, 1H,  $\text{H}^4$ ); 8.14  
743 (d, 1H,  $\text{H}^3$ ); 7.74 (d, 1H,  $\text{H}^5$ ); 7.58-7.32 (m, 4H,  $\text{H}^{\text{ar}}$ ); 7.06-6.98 (m, 2H,  $\text{H}^5 + \text{H}^7$ ); 6.78 (t, 1H,  $\text{H}^6$ );  
744 2.21 (s, 1H,  $\text{CH}_3$ ); 0.75 (s, 3H,  $^2J_{\text{Pt-H}} = 88.5$  Hz,  $\text{Pt-CH}_3$ ); 0.24 (s, 3H,  $^2J_{\text{Pt-H}} = 90.6$  Hz,  $\text{Pt-CH}_3$ ).

745

746 **[Pt(L<sup>3</sup>)(CH<sub>3</sub>)<sub>2</sub>] (19)**

747 To a solution of **L<sup>3</sup>** (0.0817 g; 0.26 mmol) in dichloromethane (25 ml) was added under vigorous  
748 stirring [Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>] (0.0992 g; 0.26 mmol). The yellow solution was stirred for 72 h at room  
749 temperature, then concentrated to a small volume and treated with diethyl ether. The precipitate  
750 formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample  
751 as a pale green solid (**19**). Yield: 0.0602 g (83%). M.p.: 225 °C

752 Found: C **51.97**; H **4.89**; N **7.61**%. Calc. for C<sub>23</sub>H<sub>25</sub>N<sub>3</sub>Pt: C, 51.29; H, 4.68; N, 7.80.

753 <sup>1</sup>H NMR, δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO]: 9.03 (d, 1H, <sup>3</sup>J<sub>Pt-H</sub> = 28.0 Hz, **H**<sup>6'</sup>); 8.32 (d, 1H, **H**<sup>8</sup>); 8.21 (t, 1H, **H**<sup>4'</sup>); 8.16  
 754 (d, 1H, **H**<sup>3'</sup>); 7.59 (d, 1H, **H**<sup>5</sup>); 7.37-7.31 (m, 2H, **H**<sup>5'</sup>+**H**<sup>7</sup>); 7.08 (s, 2H, **H**<sup>ar</sup>); 7.02 (m, 1H, **H**<sup>6</sup>); 2.38  
 755 (s, 3H, **para** CH<sub>3</sub>); 2.01 (s, 6H, **ortho** CH<sub>3</sub>); 0.77 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub> = 88.5 Hz, **Pt-CH**<sub>3</sub>); 0.28 (s, 3H, <sup>2</sup>J<sub>Pt-</sub>  
 756 H = 90.6 Hz, **Pt-CH**<sub>3</sub>).

757

### 758 [Pt(L<sup>4</sup>)(CH<sub>3</sub>)<sub>2</sub>] (**20**)

759 To a solution of **L**<sup>4</sup> (0,0372 g; 0,13 mmol) in acetone (25 ml) was added under vigorous stirring  
 760 [Pt(CH<sub>3</sub>)<sub>2</sub>(DMSO)<sub>2</sub>] (0,0496 g; 0,13 mmol). The solution was stirred for 72 h at room temperature,  
 761 then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered  
 762 off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale yellow  
 763 solid (**20**). (Found: C **50.51**; H **4.62**; N **8.03**%. Calc. for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>Pt: C, 49.41; H, 4.15; N, 8.23.

764 Yield: 0,0504 g (76%). M.p.: 227 °C

765 <sup>1</sup>H NMR, δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO]: 9.04 (d, 1H, <sup>3</sup>J<sub>Pt-H</sub> = 28.4 Hz, **H**<sup>6'</sup>); 8.16 (pt, 2H, **H**<sup>4'</sup>+**H**<sup>8</sup>); 8.10 (d, 2H,  
 766 **H**<sup>5</sup>+**H**<sup>3'</sup>); 7.44-7.26 (m, 5H, **H**<sup>ar</sup>); 7.24-7.19 (m, 2H, **H**<sup>5'</sup>+**H**<sup>7</sup>); 6.91 (t, 1H, **H**<sup>6</sup>); 4.90 (s, 2H, **CH**<sub>2</sub>);  
 767 1.10 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub> = 87.0 Hz, **Pt-CH**<sub>3</sub>); 0.91 (s, 3H, <sup>2</sup>J<sub>Pt-H</sub> = 87.9 Hz, **Pt-CH**<sub>3</sub>).

768

### 769 *Computational methods*

770 All geometry optimizations and harmonic frequency calculations were performed through  
 771 Gaussian09<sup>36</sup> at DFT level of theory using the Truhlar and co-workers M06 functional<sup>37</sup> including  
 772 dispersion; the SDD basis-set including *f*-polarization functions<sup>38</sup> and pseudo-potential has been  
 773 applied for platinum while 6-311g(d,p) for the main group atoms. The solvent effect was taken into  
 774 account employing the SMD continuum model of Marenich *et al.*<sup>39</sup> This level of theory describes  
 775 with high accuracy the structures of second- and third-row transition metal compounds,<sup>40</sup> and in  
 776 particular Pt and Pd organometallic complexes.<sup>41</sup>

777

778

### 779 **References**

- 1) (a) C. Kaes, A. Katz, M.W. Hosseini, *Chem. Rev.*, 2000, **100**, 10, 3553–3590; (b) A. Bencini, V. Lippolis, *Coord. Chem. Rev.*, 2010, **254**, 2096-2180; (c) E.C. Constable, C.E. Housecroft, *Molecules* 2019, **24**, 3951 and references therein; (d) L. Calvanese, M. E. Cucciolito, A. D'Amora, G. D'Auria, A. Esposito, R. Esposito, L. Falcigno, and F. Ruffo, *Eur. J. Inorg. Chem.*, 2015, 4068-4075; (e) A. Annunziata, A. Amoresano, M. E. Cucciolito, R. Esposito, G. Ferraro, I. Iacobucci, P. Imbimbo, R. Lucignano, M. Melchiorre, M. Monti, C. Scognamiglio, A. Tuzi, D. M.Monti, A. Merlino, and F. Ruffo, *Inorg. Chem.*, 2020, **59**, 4002-4014

- 2) (a) W. Cabri, I. Candiani, A. Bedeschi, R. Santi, *Synlett.*, 1992, 871; (b) C. Bolm, M. Zehnder, D. Bur, *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 205–207; (c) C. Bolm, M. Ewald, M. Felder, G. Schlingloff, *Chem. Ber.*, 1992, **125**, 1169–1190.
- 3) B. Liu, Yu W.-L., J. Pei, S.-Y. Liu, Y.-H. Lai, W. Huang, *Macromolecules*, 2001, **34**, 7932–7940.
- 4) J. Mathieu, B. Fraisse, D. Lacour, N. Ghermani, F. Montaigne, A. Marsura, *Eur. J. Inorg. Chem.*, 2006, 133–136.
- 5) U. S. Schubert, J. L. Kersten, A.E. Pemp, C. D. Eisenbach, G. R Newkome, *Eur. J. Org. Chem.*, 1998, 2573–2581.
- 6) V. Balzani, A. Juris, *Coord. Chem. Rev.*, 2001, **211**, 97–115.
- 7) S. Margel, W. Smith, F. C. Anson, *J. Electrochem. Soc.*, 1978, **125**, 241–246.
- 8) (a) G. Minghetti, M.A. Cinellu, S. Stoccoro, G. Chelucci and A. Zucca, *Inorg. Chem.*, 1990, **29**, 5138; (b) G. Minghetti, M.A. Cinellu, S. Stoccoro, A. Zucca and M. Manassero, *J. Chem. Soc. Dalton Trans.*, 1995, 777; (c) A. Zucca, M.A. Cinellu, M.V. Pinna, S. Stoccoro, and G. Minghetti, *Organometallics*, 2000, **19**, 4295; (d) A. Zucca, S. Stoccoro, M.A. Cinellu, G. Minghetti, M. Manassero and M. Sansoni, *Eur. J. Inorg. Chem.*, 2002, 3336; (e) G. Minghetti, S. Stoccoro, M.A. Cinellu, B. Soro, and A. Zucca, *Organometallics*, 2003, **22**, 4770; (f) A. Zucca, S. Stoccoro, M.A. Cinellu, G.L. Petretto and G. Minghetti, *Organometallics*, 2007, **26**, 5621; (g) O.A. Filippov, V. A. Kirkina, N.V. Belkova, S. Stoccoro, A. Zucca, G. M. Babakhina, L.M. Epstein, and E.S. Shubina, *Z. Phys. Chem.*, 2013, **227** (6-7) 869; (h) F. Cocco, A. Zucca, S. Stoccoro, M. Serratrice, A. Guerri, and M. A. Cinellu, *Organometallics*, 2014, **33**, 3414; (i) S. Stoccoro, L. Maidich, T. Ruiu, M. A. Cinellu, G. J. Clarkson and A. Zucca, *Dalton Transactions*, 2015, **44** (41), 18001–18011; (j) L. Maidich, M.A. Cinellu, F. Cocco, S. Stoccoro, M. Sedda, S. Galli and A. Zucca *J. Organomet. Chem.*, 2016, **819**, 76.
- 9) G. Hajos; Z. Riedl, *Science of Synthesis*, 2002, **12**, 613.
- 10) (a) A. G. Ligtenbarg; A. L. Spek; R. Hage ; B. L. Feringa, *J. Chem. Soc., Dalton Trans.*, 1999, 659; (b) M. E. Bluhm; M. Ciesielski; Walter, O. Go rls, M. Do ring, *Inorg. Chem.*, 2003, **42**, 8878.
- 11) E. Yamaguchi, F. Shibahara, T. Murai, *J. Org. Chem.*, 2011, **76**, 6146–6158, and references therein.
- 12) (a) M. Nakatsuka and T. Shimamura, *Jpn. Kokai Tokkyo Koho JP 2001035664*; *Chem. Abstr.*, 2001, **134**, 170632; (b) G. Tomin-aga, R. Kohama, A. Takano, *Jpn. Kokai Tokkyo Koho JP 2001006877*; *Chem. Abstr.*, 2001, **134**, 93136; (c) D. Kitazawa, G. Tominaga, A. Takano, *Jpn. Kokai Tokkyo Koho JP 2001057292*; *Chem. Abstr.*, 2001, **134**, 200276.
- 13) H. Nakamura, H. Yamamoto, *PCT Int. Appl. WO 2005043630*; *Chem. Abstr.*, 2005, **142**, 440277.

- 14) (a) L. Salassa, A. Albertino, C. Garino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Organometallics*, 2008, **27**, 1427–1435; (b) C. Garino, T. Ruiu, L. Salassa, A. Albertino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Eur. J. Inorg. Chem.*, 2008, 3587–3591.
- 15) (a) G. Volpi, E. Priola, C. Garini, A. Daolio; R. Rabezzana, P. Benzi, A. Giordana, E. Diana, R. Gobetto, *Inorg. Chim. Acta*, 2020, 509; (b) G. A. Ardizzoia, S. Brenna, S. Durini, B. Therrien and M. Veronelli, *Eur. J. Inorg. Chem.*, 2014, 4310–4319; (c) G. A. Ardizzoia, S. Brenna, S. Durini and B. Therrien, *Polyhedron*, 2015, **90**, 214–220.
- 16) S. Durini, G. A. Ardizzoia, B. Therrien and S. Brenna, *New J. Chem.*, 2017, **41**, 3006–3014.
- 17) N. Kundu, S. M. Towsif Abtab, S. Kundu, A. Endo, S. J. Teat, M. Chaudhury, *Inorg. Chem.* 2012, **51**, 2652–2661.
- 18) A. L. Guckian, M. Doering, M. Ciesielski, O. Walter, J. Hjelm, N. M. O’Boyle, W. Henry, W. R. Browne, J. J. McGarvey, J. G. Vos, *Dalton Trans.*, 2004, 3943–3949.
- 19) K.P. Thakor, M.V. Lunagariya, B.S. Bhatt, M.N. Patel, *Luminescence* 34 (2019) 113–124; (b) L. Ronconi, P.J. Sadler, *Coord. Chem. Rev.*, 2007, **251**, 1633–1648.
- 20) (a) B. Butschke and H. Schwarz, *Chem. Sci.*, 2012, **3**, 308; (b) A. Zucca, G.L. Petretto, S. Stoccoro, M.A. Cinellu, M. Manassero, C. Manassero, G. Minghetti, *Organometallics*, 2009, **28**, 2150–2159; (c) A. Zucca, L. Maidich, M. I. Pilo, S. Pischedda, M. Sedda and S. Stoccoro, *Appl. Sci.*, 2020, **10**, 6665; (d) A. Zucca and M. I. Pilo, *Molecules* (MDPI), 2021, **26**, 328.
- 21) D.A. Kanthecha, B.S. Bhatt, M. N. Patel *Heliyon*, 2019, **5**, e01968
- 22) (a) J. Wang, L. Dyers Jr., R. Mason Jr., P. Amoyaw, X. R. Bu, *J. Org. Chem.*, 2005, **70**, 2353–2356; (b) J. Wang, R. Mason, D. Van Derveer, K. Feng, X. R. Bu, *J. Org. Chem.*, 2003, **68**, 2415–2418.
- 23) R. Grigg, P. Kennewell, V. Savic, V. Sridharan *Tetrahedron*, 1992, **47-48**, 10423–10430.
- 24) S. Albano, G. Olivo, L. Mandolini, C. Massera, F. Ugozzoli, S. Di Stefano, *J. Org. Chem.*, 2017, **82**, 3820–3825.
- 25) Z. Hu, J. Hou, J. Liu, W. Yu, J. Chang, *Org. Biomol. Chem.*, 2018, **16**, 5653–5660.
- 26) (a) A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403; (b) M. Albrecht, *Chem. Rev.*, 2010, **110**, 576.
- 27) P.K. Byers and A.J. Canty, *Organometallics*, 1990, **9**, 210–220
- 28) E. Constable, R. P.G. Henney, T. A. Leese, D. A. Tocher, *J. Chem. Soc. Chem Comm.*, 1990, 513–515.
- 29) (a) J. E. Huheey, E.A. Keiter, and R.L. Keiter in *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edition, Harper Collins, New York, USA, 1993; (b) J. B. Mann, T. L. Meek, E. T. Knight, J. F. Capitani and L. C. Allen, *J. Am. Chem. Soc.*, 2000, **122**, 5132–5137.

- 30) A. Abo-Amer, M. S. McCready, F. Zhang, and R. J. Puddephatt, *Can. J. Chem.*, 2012, **90**, 46–54 and references therein.
- 31) S. Shil, D. Bhattacharya, S. Sarkar, A. Misra, Performance of the Widely Used Minnesota Density Functionals for the Prediction of Heat of Formations, Ionization Potentials of Some Benchmarked First Row Transition Metal Complexes. *The Journal of Physical Chemistry A* 2013, **117** (23), 4945-4955.
- 32) A.I. Vogel, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical: Harlow, UK, 1989.
- 33) R. E. Riilke, J. M. Ernstring, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769-5778.
- 34) (a) C. Eaborn, K. Kundu, A. J. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1981, 933-938; (b) R. Romeo, L. Monsu Scolaro, *Inorg. Synth.*, 1998, **32**, 153; (c) R. Romeo, L. Monsu` Scolaro, N. Nastasi, B. E. Mann, G. Bruno, F. Nicolo, *Inorg. Chem.*, 1996, **35**, 7691.
- 35) E. A. Baquero, A. Rodríguez-Zúñiga, J.C. Flores, M. Temprado, E. de Jesús, *J. Organomet. Chem.*, 2019, **896**, 108–112.
- 36) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, A. J. Cross, J. B., V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, R. Austin, Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, revision D.01*. Gaussian, Inc.: Wallingford, CT, 2010.
- 37) (a) Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.*, 2008, **120** (1), 215-241; (b) Y. Zhao, D. G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Phys. Chem.* 2006, **125** (19), 194101.
- 38) A. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc-Cu, Y-Ag and La-Au. *Chemical physics letters* 1993, **208** (1-2), 111-114.
- 39) A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B*, 2009, **113** (18), 6378-6396.

- 40) (a) C. J. Cramer, Truhlar, D. G., Density functional theory for transition metals and transition metal chemistry, *Phys. Chem. Chem. Phys.* 2009, **11** (46), 10757-10816; (b) Y. Minenkov, A. Singstad, G. Occhipinti, V. R. Jensen, The accuracy of DFT-optimized geometries of functional transition metal compounds: a validation study of catalysts for olefin metathesis and other reactions in the homogeneous phase. *Dalton Transactions* 2012, **41** (18), 5526-5541.
- 41) E. A. C. Bushnell, R. J. Boyd, Assessment of Several DFT Functionals in Calculation of the Reduction Potentials for Ni-, Pd-, and Pt-Bis-ethylene-1,2-dithiolene and -Diselenolene Complexes. *The Journal of Physical Chemistry A*, 2015, **119** (5), 911-918.