



**HAL**  
open science

# N-Heterocyclic Carbene Coinage Metal Complexes Containing Naphthalimide Chromophore: Design, Structure, and Photophysical Properties

Pierre-Henri Lanoë, Btissam Najjari, Florine Hallez, Geoffrey Gontard, Hani  
Amouri

► **To cite this version:**

Pierre-Henri Lanoë, Btissam Najjari, Florine Hallez, Geoffrey Gontard, Hani Amouri. N-Heterocyclic Carbene Coinage Metal Complexes Containing Naphthalimide Chromophore: Design, Structure, and Photophysical Properties. *Inorganics*, 2017, 5 (3), pp.58. 10.3390/inorganics5030058 . hal-04056244

**HAL Id: hal-04056244**

**<https://hal.sorbonne-universite.fr/hal-04056244>**

Submitted on 3 Apr 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Article

2 **N-Heterocyclic Carbene Coinage Metal Complexes**  
3 **Containing Naphthalimide Chromophore: Design,**  
4 **Structure and Photophysical Properties**5 *Pierre Henri Lanoë, † Btissam Najjari, † Florine Hallez, † Geoffrey Gontard, † and Hani Amouri\* ‡*

6

7

8

9

10

11

12

13

14

‡ Sorbonne Universités, UPMC Univ Paris 06 and CNRS, (IPCM) UMR 8232, 4 place Jussieu, 75252 Paris cedex 05, France; Pierre Henri Lanoë, E-mail: pierre-henri.lanoë@upmc.fr, Btissam Najjari, E-mail: najjari015@gmail.com, Florine Hallez, E-mail: florine.hallez@etu.upmc.fr, Geoffrey Gontard, E-mail: geoffrey.gontard@upmc.fr

\* Author to whom correspondence should be addressed; E-mail: hani.amouri@upmc.fr.

Received: date; Accepted: date; Published: date

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

**Abstract:** A series of novel *N*-heterocyclic carbene coinage metal complexes containing a naphthalimide (NI) chromophore have been prepared and fully characterized. Two types of molecules are described those where the NI unit is directly attached to the carbene unit with the general formulae  $[(L^1)\text{-M-X}]$ ,  $M = \text{Cu}$ ,  $X = \text{Cl}$  (**1a**);  $M = \text{Ag}$ ,  $X = \text{I}$  (**1b**) and  $M = \text{Au}$ ,  $X = \text{Cl}$ , (**1c**). While in the second family a  $\pi$ -extended carbene ligand precursor  $L^2\text{H}^+ \text{I}^-$  (**3**) was prepared where the NI unit is distant from the imidazole unit via a phenyl-alkyne bridge. Only two *N*-heterocyclic carbene metal complexes were prepared  $[(L^2)\text{-M-Cl}]$ ,  $M = \text{Cu}$  (**2a**) and  $M = \text{Au}$  (**2c**). The related silver carbene compound could not be isolated. The molecular structure of the carbene complex **1c** was determined and confirmed the formation of the target compound. Interestingly the structure shows the presence of an aurophilic interaction  $\text{Au}\cdots\text{Au}$  at 3.407 Å between two individual molecules. The photophysical properties of the compounds were investigated in solution at room temperature. Preliminary results suggested that all compounds are luminescent and act as blue emitters (420–451 nm). These transition emissions can be attributed to intraligand origin of the NI chromophore. Moreover the carbene complexes featuring  $L^2$  ligand with  $\pi$ -extended system were found to be more luminescent.

30

31

**Keywords:** *N*-heterocyclic Carbenes; Coinage Metals; Photophysical Properties.

32

### 1. Introduction

33

34

35

36

37

38

39

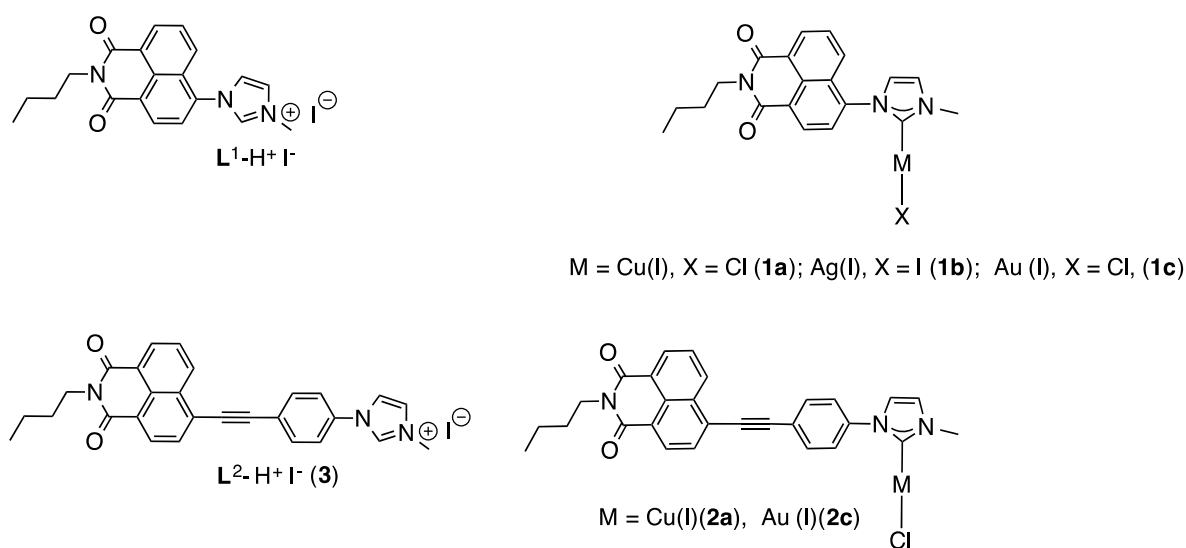
40

41

42

*N*-heterocyclic carbene (NHC) ligands have received much attention since the isolation of the free imidazole-2-ylidene ligand by *Arduengo et al.* in 1991[1]. However the first metal complexes were reported back in 1965 by Ofele and Wanzlick *et al*[2,3]. Indeed they allow the formation of stable compounds that have important applications in various fields of chemistry [4,5] such as organometallics[6], homogeneous catalysis[7], metallosupramolecular chemistry, metallodrugs[8] and more recently as luminescent materials[9–11]. In the latter a wide range of luminescent complexes were prepared displaying various properties however efforts were focused on *N*-heterocyclic coinage metal complexes because they tend to form metal–metal interactions at the supramolecular level which might add a novel property to their luminescent properties and also for their potential application as light emitting devices [12–16].

43 We recently reported the synthesis and characterization of a family of cyclometalated iridium  
 44 carbene complexes containing a naphthalimide chromophore[17]. The latter behaved as deep red  
 45 phosphorescent compounds with good quantum yields and long lifetimes. Thus we sought to  
 46 extend our approach to other metal chromophores mainly coinage metals. In fact due to their linear  
 47 geometry we expected to promote metal--metal interactions[12,18,19] and hence add a novel  
 48 property to this kind of compounds relative to the cyclometalated iridium compounds. In this paper  
 49 we describe the synthesis and photophysical properties of a novel class of *N*-heterocyclic carbene  
 50 complexes of Cu(I), Ag(I) and Au(I) containing a naphthalimide chromophore. Two types of  
 51 compounds are described (i) those where the naphthalimide is directly linked to the carbene unit,  
 52 while in the other case (ii) the organic chromophore is distant from the carbene unit *via* an alkyne  
 53 arene linkage (Figure 1).



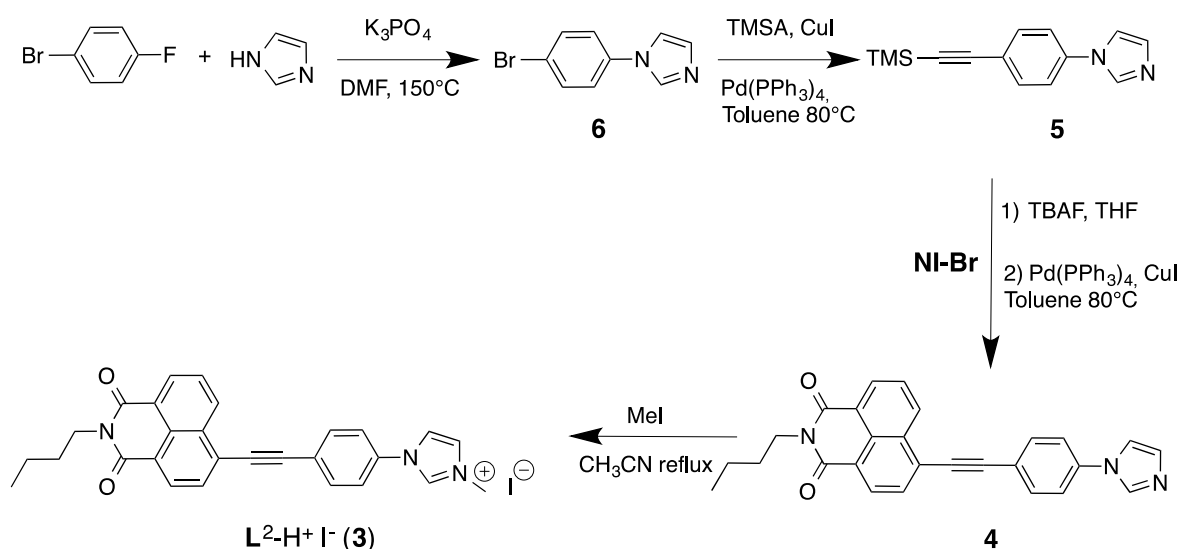
54

55 **Figure 1.** Ligand precursors  $L^1-H^+I^-$  and  $L^2-H^+I^-$  and the related NHC carbene complexes with  
 56 naphthalimide chromophore described in this work.

## 57 2. Results and Discussions

### 58 2.1 Synthesis and characterization of the imidazolium salts

59 The carbene ligand precursor  $L^1-H^+I^-$  was prepared according to our previously reported  
 60 procedure[17]. For  $L^2-H^+I^-$  containing an extended carbon skeleton, the product was prepared in  
 61 several steps. Thus reaction of imidazole with *p*-bromofluorobenzene in presence of potassium  
 62 phosphate provided 1-(4-bromophenyl)-imidazole (**6**) (scheme 1) [20]. Subsequent  
 63 Sonogashira-Hagihara cross coupling reaction in toluene gave the desired compound **5** in good yield  
 64 (90%). Cleavage of the Si-C bond using TBAF provided the free alkyne, which was directly engaged  
 65 in the next step without purification. A second Sonogashira-Hagihara cross coupling reaction  
 66 between the latter compound and naphthalimide-Br (NI-Br) led to compound **4** in good yield (78%).  
 67 The methylation reaction took place in refluxing  $CH_3CN$  with excess of MeI to form the azolium salt  
 68  $L^2-H^+I^-$  in satisfactory yield (63%). Full characterizations of these compounds are given in the  
 69 experimental section.

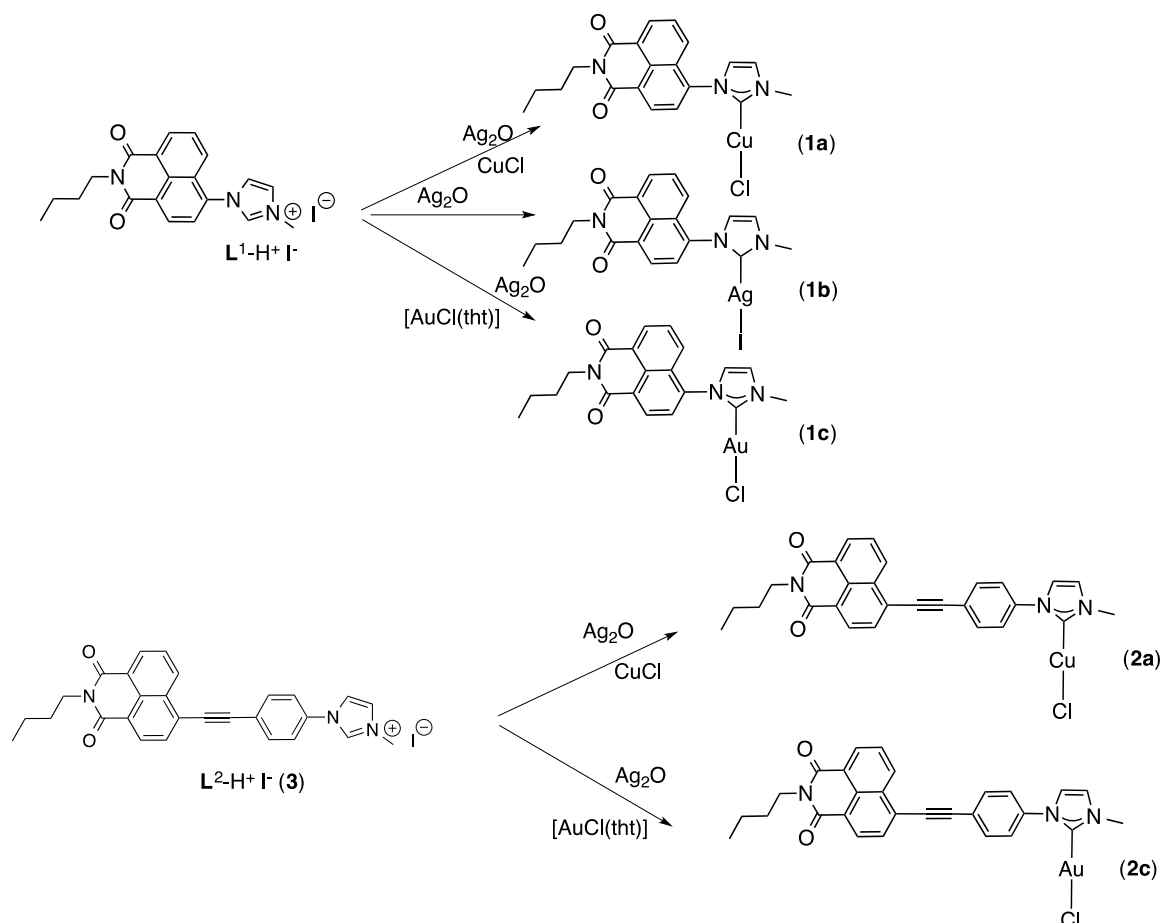


**Scheme 1.** Synthesis of the carbene ligand precursor L<sup>2</sup>-H<sup>+</sup>I<sup>-</sup> (**3**).

## 2.2 Synthesis and characterization of the NHC coinage metal complexes.

The novel coinage metal carbene complexes were obtained following the *silver carbene transfer route* as described previously in the literature [21,22]. Thus treatment of Ag<sub>2</sub>O with L<sup>1</sup>-H<sup>+</sup> I<sup>-</sup> in dry CH<sub>2</sub>Cl<sub>2</sub> solution and subsequent transmetalation with the appropriate metal sources (i.e. CuCl or (tbt)AuCl) leads to the formation of Cu(I) and Au(I) complexes in moderate to good yields [(L<sup>1</sup>)-Cu-Cl] (**1a**) (30%) [(L<sup>1</sup>)-Au-Cl] (**1c**) (72%). For comparison purposes the silver complex was also prepared [(L<sup>1</sup>)-Ag-I] (**1b**) in 94% yield.

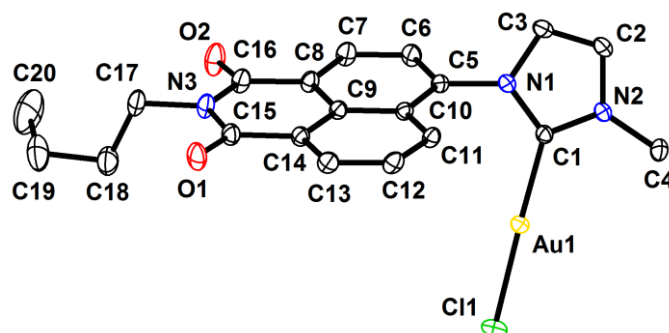
On the other hand we found that using L<sup>2</sup>-H<sup>+</sup>I<sup>-</sup> carbene precursor the reactions were more tedious and required the use of a mixture of CH<sub>3</sub>NO<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> for solubility purposes. For instance the [(L<sup>2</sup>)-Cu-Cl] (**2a**) and [(L<sup>2</sup>)-Au-Cl] (**2c**) were obtained (33%) and (72%) yield respectively after 16 hours of reaction using Ag<sub>2</sub>O precursor. Despite all our efforts we were unable to isolate the silver carbene complex [(L<sup>2</sup>)-Ag-I] (**2b**). All compounds have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, elemental analysis, moreover the X-ray molecular structure of **1c** was determined and confirmed the formation of the desired compound (*vide infra*). In particular the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the azolium salts showed the presence of a singlet for the C-H group around δ 135 ppm while the related metal carbene complexes **1b**, **1c** and **2c** displayed a singlet for the carbene carbon centers in the range of δ 171- 182 ppm.



90  
91 **Scheme 2.** Synthesis of the novel carbene coinage metal complexes.  
92

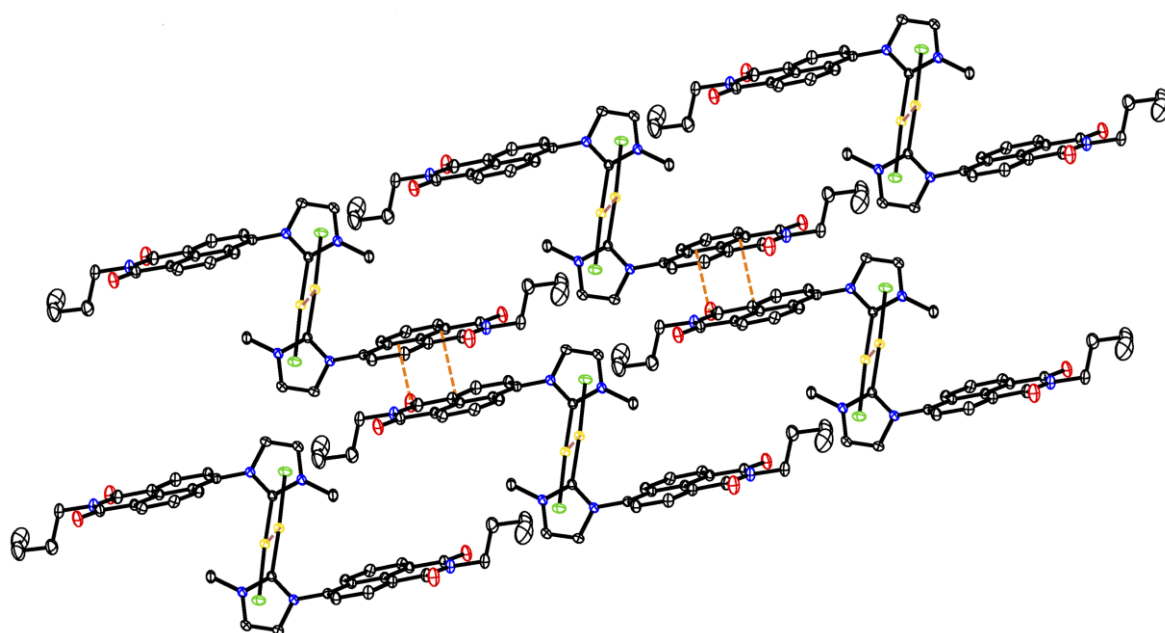
93 **2.3 X-ray molecular structure of the N-heterocyclic gold carbene complex [(L<sup>1</sup>)-Au-Cl] (1c)**

94 Convenient crystals for X-ray diffraction crystallography were grown by slow vapor diffusion  
95 of diethylether into a dichloromethane solution of [(L<sup>1</sup>)-Au-Cl] (1c) (Table S1). A view of the  
96 structure is given in Figure 2 with selected bond distances and angles. The structure confirms the  
97 formation of the target gold complex 1c. Moreover it shows the geometry around the Au(I) center is  
98 almost linear with a  $C_{\text{carbene}}-Au-Cl$  angle of approximately  $175.88(7)^\circ$ . The  $C_{\text{carbene}}-Au$  and  $Au-Cl$   
99 distances are 1.985(5) Å and 2.287(0), respectively typical to those reported for previous complexes  
100 containing a simple carbene ligand[15,23,24]. In addition, the planes of the imidazole-2-ylidene  
101 moiety and the NI moiety show an angle of approximately of  $65.81(8)^\circ$ . To our knowledge this is the  
102 first molecular structure of a gold carbene complex tethered to a naphthalimide chromophore.  
103



104  
105 **Figure 2.** View of the molecular structure of the gold carbene complex [(L<sup>1</sup>)-Au-Cl] (1c). Selected  
106 bond distances (Å) and angle ( $^\circ$ ).  $Au(1)-C(1) = 1.986(2)$ ,  $Au(1)-Cl(1) = 2.287(1)$ ,  $N(1)-C(1) = 1.353(3)$ ,  
107  $N(1)-C(3) = 1.388(3)$ ,  $N(1)-C(5) = 1.427(3)$ ,  $N(2)-C(1) = 1.338(3)$ ,  $N(2)-C(2) = 1.381(3)$ ,  $N(2)-C(4) =$   
108  $1.457(3)$ ,  $C(1)-Au(1)-Cl(1) = 175.88(7)$ ,  $N(1)-C(1)-N(2) = 105.4(2)$ .

109



110

111

**Figure 3.** Crystal packing of **1c** showing aurophilic Au---Au contact at 3.407(1) Å between two individual molecules in head to tail fashion and  $\pi$ - $\pi$  interactions at 3.40 Å between two naphthalimide units to generate a 2D supramolecular structure.

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

129

130

131

132

133

134

135

136

137

138

139

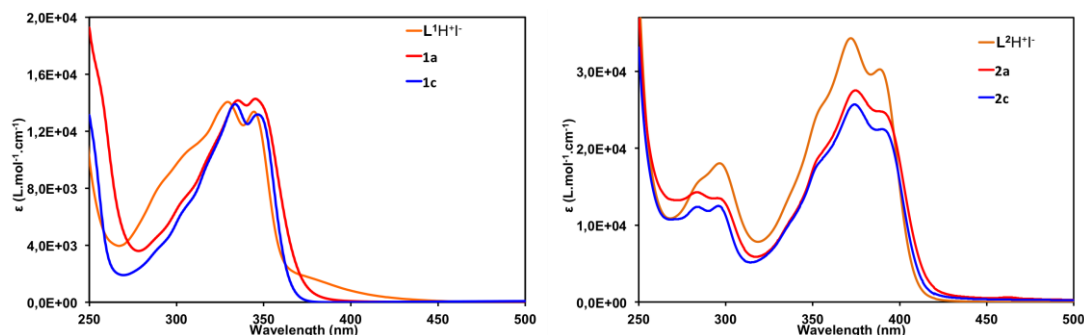
140

An examination of the crystal packing reveals that the individual molecules display Au---Au and  $\pi$ - $\pi$  interactions (Figure 3). Indeed molecules interact pairwise in head-to-tail fashion through aurophilic interactions with Au---Au distance of 3.407(1) Å. Furthermore, the molecules demonstrate additional  $\pi$ - $\pi$  interactions around 3.40 Å to form a 2D supramolecular structure. We then examined their photophysical properties.

#### 2.4 Photophysical properties.

All compounds have been studied in diluted air equilibrated  $\text{CH}_2\text{Cl}_2$  solution except for silver carbene complex  $[(\text{L}^1)\text{-Ag-I}]$  (**1b**) which was not stable in  $\text{CH}_2\text{Cl}_2$  solution and hence could not be investigated. The imidazolium salts  $\text{L}^1\text{-H}^+$  I<sup>-</sup> and  $\text{L}^2\text{-H}^+$  I<sup>-</sup> display different absorption spectra for instance the  $\text{L}^2$  series are bathochromically shifted relative to  $\text{L}^1$  series due to  $\pi$ -conjugation (Figure 3). More over they show additional absorption peaks at 280-320 nm, which are not present in the  $\text{L}^1$ -type ligand and related complexes. These bands are assigned to  $\pi \rightarrow \pi^*$  involving the acetylide unit (Figure 3). Furthermore the  $\text{L}^1\text{-H}^+$  I<sup>-</sup> and the related carbene complexes  $[(\text{L}^1)\text{-Cu-Cl}]$  (**1a**) and  $[(\text{L}^1)\text{-Au-Cl}]$  (**1c**), show a broad absorption band between 300 nm and 400 nm ( $12.0 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1} < \epsilon < 15.3 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), which might be a superposition of at least two bands, (Figure 4 and table 1). These bands might be attributed to  ${}^1n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions which are in agreement to those reported for the functionalized naphthalimide chromophore[25]. Remarkably the azolium salt  $\text{L}^1\text{-H}^+$  I<sup>-</sup> displayed a long tail up to 450 nm reminiscent of an aggregation phenomenon that is occurring in  $\text{CH}_2\text{Cl}_2$ . Indeed we then recorded the UV visible spectrum of  $\text{L}^1\text{-H}^+$  I<sup>-</sup> at the same concentration but in  $\text{CH}_3\text{CN}$  instead (Figure S1) which showed the disappearance of this low energy band. Such aggregation phenomena have been reported previously to other functionalized naphthalimide system[26].

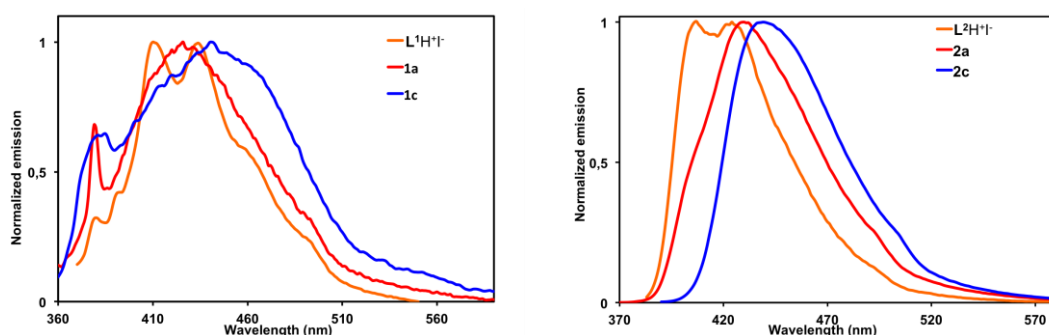
As for the azolium salt  $\text{L}^2\text{-H}^+$  I<sup>-</sup> (**3**) and the related carbene complexes  $[(\text{L}^2)\text{-Cu-Cl}]$  (**2a**) and  $[(\text{L}^2)\text{-Au-Cl}]$  (**2c**), this broad absorption band appears between 320nm and 430nm and is red shifted compared to the previous compounds we also note that the molar absorptivity is higher.



141  
142  
143 **Figure 4.** Absorption spectra for the azolium salts of  $L^1-H^+I$ ,  $L^2-H^+I$  and the carbene metal  
144 complexes **1a-2a** and **1c-2c** in  $CH_2Cl_2$  solution at room temperature.

145  
146 Both features can be explained by the extended  $\pi$ -conjugation as a result of the to the presence  
147 of the phenyl-ethynyl bridge between the carbene unit and the naphthalimide (NI) chromophore.  
148

149 Preliminary results showed that the metal complexes **1a-2a** and **1c-2c** are luminescent at room  
150 temperature in  $CH_2Cl_2$  solution and displayed blue emissions in the range of 420 to 451 nm (Table 1).  
151 For instance the metal complexes containing  $L^1$ -type ligand showed a slight red shift emission  
152 relative to free to the azolium salt  $L^1-H^+I$  (Figure 4). Similarly the carbene metal complexes with  
153  $L^2$ -type ligand showed also a slight red shift relative to the free ligand  $L^2-H^+I$ . These emissions are  
154 clearly intraligand interactions centered at the naphthalimide moiety. Similar results were reported  
155 for coinage carbene complexes displaying organic chromophores[12,15,23].  
156  
157



158  
159  
160 **Figure 5.** Normalized emission for the azolium salts of  $L^1-H^+I$ ,  $L^2-H^+I$  and the carbene metal  
161 complexes **1a-2a** and **1c-2c** in  $CH_2Cl_2$  solution at room temperature.

162  
163 On the other hand we found that the complexes with  $L^2$ -type ligand displayed higher quantum  
164 yields (Table 1). Further studies at low temperature and in solid state will be conducted on these  
165 compounds in order to better understand their optical behavior.  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176

177

Compound	$\lambda_{\text{abs}}/\text{nm}$ ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1} \times 10^3$ )	$\lambda_{\text{em}}/\text{nm}$ ( $\phi_{\text{fluor}}^{\text{a}}$ )
$\text{L}^1\text{-H}^+\text{I}$	330 (14.0) 345 (13.3)	410 <sup>b</sup> , 430 (0.21) <sup>c</sup>
$[(\text{L}^1)\text{-Cu-Cl}]$ ( <b>1a</b> )	332 (13.8); 346 (14.2)	426 (0.07) <sup>c</sup>
$[(\text{L}^1)\text{-Au-Cl}]$ ( <b>1c</b> )	335 (13.7); 349 (12.9)	451 (0.01) <sup>c</sup>
$\text{L}^2\text{-H}^+\text{I}$ ( <b>3</b> )	285 (15.8); 296 (18.0); 372 (34.3); 389 (30.2)	406, 424 <sup>b</sup> (0.73) <sup>d</sup>
$[(\text{L}^2)\text{-Cu-Cl}]$ ( <b>2a</b> )	284 (14.2); 299 (13.2); 376 (13.2); 3393 (24.2)	428 (0.20) <sup>d</sup>
$[(\text{L}^2)\text{-Au-Cl}]$ ( <b>2c</b> )	284 (12.4); 298 (12.1); 375 (25.6); 393 (21.9)	429 (0.29) <sup>d</sup>

178

179

180 **Table 1.** Absorption and emission data for the azolium salts of  $\text{L}^1$  and  $\text{L}^2$ , and the carbene metal  
 181 complexes **1a-2a** and **1c-2c** from  $\text{CH}_2\text{Cl}_2$  solutions at room temperature. a) Quantum yields (QYs)  
 182 have been estimated by taking 9,10-diphenylanthracene in cyclohexane as a reference with QY =  
 0,90[27]. b)  $\lambda_{\text{max}}$  c)  $\lambda_{\text{exc}} = 340$  nm. d)  $\lambda_{\text{exc}} = 350$  nm.

183

## 2.5 Concluding remarks

184

185

186

187

188

189

190

191

192

193

194

195

In this work we reported the synthesis of first family of coinage metal complexes containing a chromophoric *N*-heterocyclic carbene ligands. For comparison purposes, two types of compounds were prepared those where the carbene unit is directly linked to the naphthalimide chromophore  $[(\text{L}^1)\text{-M-Cl}]$ ,  $\text{M} = \text{Cu}$  (**1a**),  $\text{M} = \text{Ag}$ , (**1b**) and  $\text{M} = \text{Au}$  (**1c**) while in the second series the chromophore is moved away via an alkyne-arene linkage  $[(\text{L}^2)\text{-M-Cl}]$ ,  $\text{M} = \text{Cu}$  (**2a**),  $\text{M} = \text{Au}$ , (**2c**). The X-ray molecular structure of the gold carbene complex **1c** was determined and showed the presence of aurophilic interaction. Preliminary results suggest that these compounds are luminescent at room temperature and act as blue emitters. Moreover the complexes with extended  $\pi$ -skeleton were found to be more luminescent. Our efforts are currently devoted to extend this methodology to related coinage complexes containing carbon-donor ligands instead of the halogen groups to improve their quantum yields and seek applications as organic light emitting diodes.



196 **3. Experimental section**

## 197 General experimental methods

198 Commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI  
199 Chemical, Strem or Fluorochem and used as received unless otherwise specified. Solvents were obtained from  
200 same commercial sources and used without further purification unless otherwise specified. Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub> and  
201 Et<sub>2</sub>O were distilled respectively on sodium, CaH<sub>2</sub> and sodium/benzophenon. Toluene was stored over 4 Å  
202 molecular sieve under Ar. Copper(I) chloride has been prepared according to a reported procedure[28] and  
203 stored in a Schlenk tube under Ar. Glassware was oven-dried prior to use. <sup>1</sup>H NMR spectra were recorded on a  
204 300 MHz and on a 400 MHz in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or (CD<sub>3</sub>)<sub>2</sub>SO and data are reported as follows: chemical shift in  
205 ppm from tetramethylsilane with the solvent as an internal indicator (CDCl<sub>3</sub> 7.26 ppm, CD<sub>2</sub>Cl<sub>2</sub> 5.32 ppm and  
206 (CD<sub>3</sub>)<sub>2</sub>SO 2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet or  
207 overlap of non-equivalent resonances), integration. <sup>13</sup>C NMR spectra were recorded either on a 75.4 MHz or on  
208 a 101 MHz in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or (CD<sub>3</sub>)<sub>2</sub>SO and data are reported as follows: chemical shift in ppm from  
209 tetramethylsilane with the solvent as an internal indicator (CDCl<sub>3</sub> 77.16 ppm, CD<sub>2</sub>Cl<sub>2</sub> 53.84 ppm and (CD<sub>3</sub>)<sub>2</sub>SO  
210 39.52 ppm). Absorption measurement has been performed on a Jasco V-670 and luminescence measurement on  
211 a Jasco FP-8300 Fluorometer.

212  
213 Synthesis of compound 5

214 In an oven-dried Schlenk tube under Ar atmosphere, 1-(4-Bromophenyl)-imidazole 6 (2 g, 8.97 mmol), CuI (51  
215 mg, 0.27 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (189 mg, 0.27 mmol) were introduced in a mixture of toluene (15 mL) and  
216 Et<sub>3</sub>N (2 mL). The solution was degassed three times using freeze-pump-thaw technique. TMSA (1 mL, 6.72  
217 mmol) was added to the solution and heated at 80 °C overnight (16h). The mixture was then heated at 50 °C and  
218 solvents were evaporated to dryness. At r.t., the dark crude material was treated with Et<sub>2</sub>O and the suspension  
219 was filtrated on Dicalite®. The solvent was evaporated and a column chromatography (SiO<sub>2</sub>,  
220 ethylacetate/cyclohexane from 7/3 to 1/0) to give a greyish compound 5 (1.953 g, 90%). <sup>1</sup>H NMR (300 MHz,  
221 CDCl<sub>3</sub>) δ 7.86 (s, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.28 (s, 1H), 7.21 (s, 1H), 0.26 (s, 9H). <sup>13</sup>C{<sup>1</sup>H}  
222 NMR (75 MHz, CDCl<sub>3</sub>) δ 137.1, 135.6, 133.7, 130.9, 122.6, 121.1, 118.0, 103.8, 96.0, 0.1. Analysis Calcd. for  
223 C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>Si.1/10CH<sub>2</sub>Cl<sub>2</sub> : C, 68.05; H, 6.56; N, 11.26; found C, 68.48 ; H, 6.92; N, 11.09.

224  
225 Synthesis of compound 4

226 Tetrabutylammonium fluoride monohydrate (1.153 g, 4.41 mmol) was added to a solution of compound 5 (1 g,  
227 4.16 mmol) in THF (25 mL). The reaction was monitored by TLC (SiO<sub>2</sub>, ethylacetate) and after full conversion,  
228 deionized water (20 mL) was added and the aqueous phase was extracted three times with Et<sub>2</sub>O. The combined  
229 organic layers were washed two times with brine, dried over MgSO<sub>4</sub> and solvents were removed under reduce  
230 pressure. The crude product was engaged in the next step without further purification. In a dry Schlenk tube  
231 under Ar, the crude alkyne (603 mg, 3.59 mmol), 4-bromonaphtalimide (1.312 g, 3.95 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (126  
232 mg, 0.18 mmol) and CuI (34 mg, 0.18 mmol) were dissolved/suspended in a mixture of toluene (20 mL) and  
233 Et<sub>3</sub>N (2 mL). The solution was degassed three times. The mixture was then heated at 80 °C and the reaction was  
234 monitored by TLC (SiO<sub>2</sub>, ethylacetate/C<sub>6</sub>H<sub>12</sub>). After full conversion (roughly 2hrs), the solvents were removed  
235 and the dark material was treated with CH<sub>2</sub>Cl<sub>2</sub>. The dark solution was filtrated on Dicalite® and the solvents  
236 were removed under reduce pressure. A chromatography column was performed (SiO<sub>2</sub>, from pure CH<sub>2</sub>Cl<sub>2</sub> to  
237 CH<sub>2</sub>Cl<sub>2</sub>/MeOH 7/3). The fractions containing the compound were combined and the solvent was removed  
238 under vacuum. The yellow solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed 3 times with a solution of K<sub>2</sub>CO<sub>3</sub> (1 N) and  
239 dried over MgSO<sub>4</sub>. After evaporation of the solvent, the compound was obtained as yellow solid (1,175 g, 78%).  
240 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.70 (dd, J = 8.4 Hz, J = 1.1 Hz, 1H), 8.64 (dd, J = 7.3 Hz, J = 1.2 Hz, 1H), 8.56 (d, J =  
241 7.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.94 (s, 1H), 7.84 (dd, J = 8.4 Hz, J = 7.3 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.48  
242 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 1.4 Hz, 1H), 4.35 – 4.03 (m, 2H), 1.86 – 1.64 (m, 2H), 1.45 (h, J = 7.3 Hz, 2H), 0.99 (d,  
243 J = 7.3 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 164.0, 163.8, 137.9, 135.5, 133.7, 132.2, 131.8, 131.7, 131.2, 131.1,  
244 130.4, 128.2, 127.7, 127.1, 123.3, 122.6, 121.6, 121.4, 118.0, 97.6, 87.6, 40.5, 30.4, 20.5, 14.0. Analysis calcd. for  
245 C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>.1/4H<sub>2</sub>O: C, 76.49; H, 5.11; N, 9.91; found C, 76.45; H, 5.04; N, 9.95.

246  
247 Synthesis of L<sup>2</sup>-H<sup>+</sup> I (3)

248 To a hot solution of 4 (156 mg, 0.37 mmol) in distilled CH<sub>3</sub>CN (20 mL) was added MeI (170 μL, 2.6 mmol) and  
249 the solution was refluxed overnight. The solvent was evaporated to dryness and the crude material was stirred  
250 30 min with Et<sub>2</sub>O (40 mL). The solution was then filtered on a frit and the brown solid was wash three times  
251 with a small amount of Et<sub>2</sub>O to give a brown solid (133 mg, 63 %). <sup>1</sup>H NMR (300 MHz, DMSO) δ 9.90 (s, 1H),

252 8.86 (d,  $J = 8.3$  Hz, 1H), 8.61 (d,  $J = 7.2$  Hz, 1H), 8.53 (d,  $J = 7.6$  Hz, 1H), 8.42 (s, 1H), 8.21 – 8.09 (m, 3H), 8.09 – 7.89  
253 (m, 4H), 4.08 (t,  $J = 7.4$  Hz, 2H), 4.00 (s, 3H), 1.66 (p,  $J = 15.3$  Hz,  $J = 7.7$  Hz, 2H), 1.39 (h,  $J = 7.5$  Hz, 2H), 0.96 (t,  $J =$   
254 7.3 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, DMSO)  $\delta$  163.1, 162.8, 136.2, 135.1, 133.7, 131.9, 131.3, 130.8, 129.9, 128.4,  
255 127.3, 125.5, 124.6, 122.7, 122.4, 122.0, 120.7, 96.9, 87.8, 36.2, 29.6, 19.8, 13.7. Analysis Calcd. for  
256  $\text{C}_{28}\text{H}_{24}\text{IN}_3\text{O}_2 \cdot 1/10\text{Et}_2\text{O}$ , C, 59.97; H, 4.43; N, 7.39; found C, 59.85; H, 4.18; N, 7.34.

### 257 258 Synthesis of Complex 1b

259 An oven-dried Schlenk under Ar was loaded with  $\text{L}^1\text{-H}^+\text{I}^-$  (143 mg, 0.3 mmol) and  $\text{Ag}_2\text{O}$  (38 mg, 0.17 mmol) and  
260 the solids were suspended in a mixture of distilled  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (1/1, 20 mL). The solution was stirred  
261 during 4-5h and protected from light using aluminum foil. Then a pinch of active carbon was added and the  
262 solution was filtered on Dicalite® and washed with a small amount of  $\text{CH}_2\text{Cl}_2$ . The solution was reduced under  
263 vacuum, subsequent addition of  $\text{Et}_2\text{O}$  provided a precipitate. The supernatant was filtered off with a cannula  
264 and the solid was dried under vacuum. **1b** was obtained as a green solid (96 mg, 94%).  $^1\text{H}$  NMR (400 MHz,  
265 DMSO)  $\delta$  8.48 (d,  $J = 7.2$  Hz, 1H), 8.34 (dd,  $J = 7.7, 2.1$  Hz, 1H), 7.93 – 7.75 (m, 5H), 4.12 – 4.05 (m, 3H), 3.88 (s, 2H),  
266 1.65 (p,  $J = 7.5$  Hz, 2H), 1.38 (h,  $J = 7.3$  Hz, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, DMSO)  $\delta$  182.8,  
267 162.9, 162.4, 140.7, 131.3, 130.1, 128.7, 128.5, 127.8, 126.9, 125.6, 124.3, 123.9, 122.5, 122.2, 29.5, 19.8, 13.7. Analysis  
268 Calcd. for  $\text{C}_{20}\text{H}_{19}\text{AgIN}_3\text{O}_2 \cdot \text{CH}_2\text{Cl}_2$ , C, 38.62; H, 3.24; N, 6.43; found C, 38.64; H, 2.98; N, 6.63.

### 269 General procedure for the synthesis of 1a and 1c

270 An oven-dried Schlenk under Ar was loaded with the imidazolium salt (1 eq.) and  $\text{Ag}_2\text{O}$  (from 0.5 eq. to 0.56  
271 eq.) and the solids were suspended in a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (1/1). The solution was stirred 4-5h  
272 under light protection using aluminum foil. Then a pinch of active carbon was added and the solution was  
273 filtered with a cannula fitted with a filter paper and the black solid washed with a small amount of  $\text{CH}_2\text{Cl}_2$ . The  
274 solution was reduced under vacuum subsequent addition of  $\text{Et}_2\text{O}$  provided a precipitate. The supernatant was  
275 filtrate off with a cannula fitted with a filter paper and the solid was dried under vacuum. The desired metal salt  
276 was then added to the crude  $\text{Ag(I)}$  complex in  $\text{CH}_2\text{Cl}_2$ . The solution was stirred overnight at r.t. The yellowish  
277 precipitate was filtered off with a cannula fitted with a filter paper. The solid was washed two times with  
278  $\text{CH}_2\text{Cl}_2$  and the solution was concentrated under vacuum, subsequent addition of  $\text{Et}_2\text{O}$  provided the desired  
279 complex which was separated and dried.

### 280 For complex 1a

281  $\text{L}^1\text{-H}^+\text{I}^-$  (95 mg, 0.2 mmol),  $\text{Ag}_2\text{O}$  (26 mg, 0.11 mmol) and  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (14 mL).  $\text{CuCl}$  (20 mg, 0.2 mmol) and  
282  $\text{CH}_2\text{Cl}_2$  (10 mL). The complex was obtained as an yellow solid (22 mg, 30%). Analysis calcd for  $\text{C}_{20}\text{H}_{19}\text{CuClIN}_3\text{O}_2$   
283  $\cdot 1/4\text{CH}_2\text{Cl}_2$ : C, 53.62; H, 4.33; N, 9.26; found, C, 53.70; H, 4.57; N, 8.99.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.77 – 8.64  
284 (m, 2H), 8.00 (dd,  $J = 8.5$  Hz,  $J = 1.2$  Hz, 1H), 7.92 – 7.80 (m, 2H), 7.33 (s, 1H), 7.27 (s, 1H), 4.22 – 4.12 (m, 2H), 4.03  
285 (s, 3H), 1.81 – 1.61 (m, 2H), 1.45 (h,  $J = 7.4$  Hz,  $J = 7.3$  Hz, 2H), 0.99 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  
286  $\text{CD}_2\text{Cl}_2$ )  $\delta$  164.0, 163.4, 132.3, 131.0, 129.5, 128.8, 128.7, 128.1, 126.1, 124.5, 123.9, 40.7, 30.5, 20.8, 14.0.

### 287 288 For complex 1c

289  $\text{L}^1\text{-H}^+\text{I}^-$  (95 mg, 0.2 mmol),  $\text{Ag}_2\text{O}$  (23 mg, 0.1 mmol) and  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (14 mL).  $(\text{tht})\text{AuCl}$  (64 mg, 0.2 mmol)  
290 and  $\text{CH}_2\text{Cl}_2$  (10 mL). The complex was obtained as an off white solid (73 mg, 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$   
291 8.68 (d,  $J = 7.7$  Hz, 1H), 8.67 (dd,  $J = 7.0$  Hz,  $J = 1.4$  Hz, 1H), 7.94 – 7.79 (m, 3H), 7.31 (s, 2H), 4.18 (t,  $J = 7.6$  Hz, 2H),  
292 4.02 (s, 3H), 1.79 – 1.67 (m, 2H), 1.45 (h,  $J = 7.5$  Hz, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$   
293 173.9, 163.9, 163.4, 140.4, 132.3, 130.8, 129.3, 128.8, 128.6, 128.4, 126.8, 124.8, 123.8, 123.7, 123.0, 40.7, 39.0, 30.5,  
294 20.7, 14.0. Analysis calcd for  $\text{C}_{20}\text{H}_{19}\text{AuClIN}_3\text{O}_2 \cdot 1/4\text{CH}_2\text{Cl}_2$ : C, 41.43; H, 3.35; N, 7.43; found, C, 41.00; H, 3.17;  
295 N, 7.19.

### 296 297 General procedure for the synthesis of 2a and 2c

298 In an oven-dried Schlenk tube protected from light with aluminum foil, iodide salt and  $\text{Ag}_2\text{O}$  were suspended  
299 in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{NO}_2$  mixture (4/1, v/v). After 5-6h, a yellow suspension was formed and the desired metal  
300 precursor (whether  $(\text{tht})\text{AuCl}$  or  $\text{CuCl}$ ) was added to the suspension. After 12-16h of stirring, the solution was  
301 filtered off with a cannula and the filtrate was separated into a Schlenk tube as translucent yellow solution. The  
302 remaining solid was washed three times with  $\text{CH}_2\text{Cl}_2$  and the filtrate was concentrated under vacuum  
303 subsequent  $\text{Et}_2\text{O}$  addition provided a precipitate, the mixture was then allowed to stand in a freezer for several  
304 hours. The supernatant was filtered off with a cannula fitted with a filter paper and the yellow solid was dried  
305 under vacuum.

### 306 307 For Complex 2a

308 L<sup>2</sup>-H<sup>+</sup>I<sup>-</sup> (84 mg, 0.15 mmol), Ag<sub>2</sub>O (19 mg, 0.08 mmol), CuCl (15 mg, 0.15 mmol), CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and MeNO<sub>2</sub> (5  
309 mL). The complex was obtained as a yellow solid (53 mg, 63%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.77 (dd, *J* = 8.4  
310 Hz, *J* = 1.2 Hz, 1H), 8.63 (dd, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 8.55 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.94 – 7.83  
311 (m, 3H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 1.6 Hz, 1H), 7.20 – 7.06 (m, 1H), 4.22 – 4.12 (m, 2H), 3.98 (s, 3H), 1.71  
312 (p, *J* = 7.5 Hz, 2H), 1.45 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.2, 164.0,  
313 140.5, 133.7, 132.5, 132.1, 131.8, 131.4, 130.5, 128.5, 128.1, 127.2, 124.4, 123.7, 123.3, 123.2, 121.2, 97.6, 88.2, 40.6,  
314 39.2, 30.6, 20.8, 14.1. Analysis calcd for C<sub>28</sub>H<sub>23</sub>ClCuN<sub>3</sub>O<sub>2.4</sub>/10CH<sub>2</sub>Cl<sub>2</sub>: C, 60.22; H, 4.23; N, 11.22, found C, 60.13;  
315 H, 4.11; N, 7.81.

316

317 For Complex 2c

318 L<sup>2</sup>-H<sup>+</sup>I<sup>-</sup> (102 mg, 0.18 mmol), Ag<sub>2</sub>O (23 mg, 0.10 mmol), (tht)AuCl (58 mg, 0.18 mmol), CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and  
319 MeNO<sub>2</sub> (5 mL). The complex was obtained as a yellow solid (38 mg, 33%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.77  
320 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 8.63 (dd, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 8.55 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H),  
321 7.94 – 7.83 (m, 3H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 1.6 Hz, 1H), 7.20 – 7.06 (m, 1H), 4.22 – 4.12 (m, 2H), 3.98 (s,  
322 3H), 1.71 (p, *J* = 7.5 Hz, 2H), 1.45 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ  
323 171.6, 164.2, 163.9, 139.9, 133.6, 133.4, 132.5, 132.0, 131.8, 131.4, 130.4, 128.4, 128.0, 127.1, 125.5, 125.4, 123.7, 123.6,  
324 123.1, 121.8, 115.4, 97.4, 88.2, 40.5, 39.2, 30.5, 20.8, 14.0. Analysis calcd for C<sub>28</sub>H<sub>23</sub>ClAuN<sub>3</sub>O<sub>2</sub>: C, 50.50; H, 3.48; N,  
325 6.31, found C, 50.09; H, 3.39; N, 6.35.

326

327 X-Ray crystal structure determination.

328 A single crystal of [(L<sup>1</sup>)-Au-Cl] (1c) was selected, mounted and transferred into a cold nitrogen gas stream.  
329 Intensity data was collected with a Bruker Kappa-APEX2 system using fine-focus sealed-tube radiation.  
330 Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried  
331 out with the Bruker APEX2 suite of programs. The structure was solved with SHELXT-2014<sup>C1</sup> and refined  
332 anisotropically by full-matrix least-squares methods with SHELXL-2014[29] using the WinGX suite[30].  
333 Relevant data was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1558193 and  
334 can be obtained free of charge via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

335

336 Crystal data for (1c).

337 yellow prism, C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>ClAu, triclinic P-1, *a* = 9.3874(1) Å, *b* = 9.8339(2) Å, *c* = 12.0913(2) Å, α = 69.669(1)°, β =  
338 70.888(1)°, γ = 76.465(1)°, *V* = 979.82(3) Å<sup>3</sup>, *Z* = 2, *T* = 200(1) K, λ = 0.71073 Å, μ = 7.663 mm<sup>-1</sup>, min / max  
339 transmission = 0.36 / 0.84, θ range = 2.23° to 30.58°, 29802 reflections measured, 5978 independent (*R*<sub>int</sub> = 0.0187),  
340 5540 observed [*I* > 2σ(*I*)], completeness = 0.996, 246 parameters, 0 restraints, final *R* indices *R*1 [*I* > 2σ(*I*)] = 0.0209  
341 and *wR*2 (all data) = 0.0520, GOF on *F*<sup>2</sup> = 1.089, largest difference peak / hole = 2.07 / -0.59 e.Å<sup>-3</sup>.

342

343

344 Supplementary Materials: The following are available online at [www.mdpi.com/link](http://www.mdpi.com/link), Table S1:  
345 crystallographic data for complex [(L<sup>1</sup>)-Au-Cl] (1c), Figure S1: Absorption spectrum of the azolium  
346 salt L<sup>1</sup>-H<sup>+</sup> I<sup>-</sup> in CH<sub>3</sub>CN versus CH<sub>2</sub>Cl<sub>2</sub> solution at same concentration and at room temperature.

347 Acknowledgments: We thank CNRS, Centre National de la Recherche Scientifique and Sorbonne Universités,  
348 UPMC, Univ. Paris 06 for supporting this work.

349

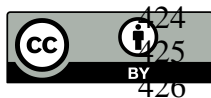
350 Conflicts of Interest: The authors declare no conflict of interest.

351

352 **Reference**

- 353 1. Arduengo, A.J.; Harlow, R.L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*,  
354 361-363.
- 355 2. Ofele, K. A New Transition-Metal Carbon Complex 1,3-Dimethyl-4-Imidazolinyliid-2-Ene  
356 Pentacarbonylchromium. *J. Organomet. Chem.* **1968**, *12*, 42-43.
- 357 3. Wanzlick, H.W.; Schonher, H.J. Direct Synthesis of a Mercury Salt-Carbene Complex. *Angew. Chem.*  
358 *Inter. Ed.* **1968**, *7*, 141-142.
- 359 4. Huynh, H.V. *The Organometallic Chemistry of N-Heterocyclic Carbenes* Wiley: Chichester, UK,  
360 2017.
- 361 5. Mercks, L.; Albrecht, M. Beyond catalysis: N-heterocyclic carbene complexes as components for  
362 medicinal, luminescent, and functional materials applications. *Chem. Soc. Rev.* **2010**, *39*, 1903-1912.
- 363 6. de Fremont, P.; Marion, N.; Nolan, S.P. Carbenes: Synthesis, properties, and organometallic  
364 chemistry. *Coord. Chem. Rev.* **2009**, *253*, 862-892.
- 365 7. Herrmann, W.A. N-heterocyclic carbenes: A new concept in organometallic catalysis. *Angew. Chem.*  
366 *Inter. Ed.* **2002**, *41*, 1290-1309.
- 367 8. Hindi, K.M.; Panzner, M.J.; Tessier, C.A.; Cannon, C.L.; Youngs, W.J. The Medicinal Applications of  
368 Imidazolium Carbene-Metal Complexes. *Chem. Rev.* **2009**, *109*, 3859-3884.
- 369 9. Visbal, R.; Gimeno, M.C. N-Heterocyclic carbene metal complexes: photoluminescence and  
370 applications. *Chem. Soc. Rev.* **2014**, *43*, 3551-3574.
- 371 10. Moussa, J.; Freeman, G.R.; Williams, J.A.G.; Chamoreau, L.M.; Herson, P.; Amouri, H. Synthesis and  
372 Luminescence Properties of Cycloplatinated Complexes with a Chelating N ^ C Pyridine-Derived  
373 N-Heterocyclic Carbene - Influence of 2,4,6-Triphenylphosphinine versus Triphenylphosphine. *Eur.*  
374 *J. Inorg. Chem.* **2016**, 761-767.
- 375 11. Moussa, J.; Haddouche, K.; Chamoreau, L.M.; Amouri, H.; Williams, J.A.G. New N ^ C ^  
376 N-coordinated Pd(II) and Pt(II) complexes of a tridentate N-heterocyclic carbene ligand featuring a  
377 6-membered central ring: synthesis, structures and luminescence. *Dalton Trans.* **2016**, *45*,  
378 12644-12648.
- 379 12. Chow, A.L.F.; So, M.H.; Lu, W.; Zhu, N.Y.; Che, C.M. Synthesis, Photophysical Properties, and  
380 Molecular Aggregation of Gold(I) Complexes Containing Carbon-Donor Ligands. *Chem. Asian J.*  
381 **2011**, *6*, 544-553.
- 382 13. Lin, J.C.Y.; Huang, R.T.W.; Lee, C.S.; Bhattacharyya, A.; Hwang, W.S.; Lin, I.J.B. Coinage  
383 Metal-N-Heterocyclic Carbene Complexes. *Chem. Rev.* **2009**, *109*, 3561-3598.
- 384 14. Lin, I.J.B.; Vasam, C.S. Review of gold(I) N-heterocyclic carbenes. *Can. J. Chem. Rev. Can.* **2005**, *83*,  
385 812-825.
- 386 15. Kriechbaum, M.; Winterleitner, G.; Gerisch, A.; List, M.; Monkowius, U. Synthesis, Characterization  
387 and Luminescence of Gold Complexes Bearing an NHC Ligand Based on the  
388 Imidazo[1,5-a]quinolinol Scaffold. *Eur. J. Inorg. Chem.* **2013**, *2013*, 5567-5575.
- 389 16. Hong, E.Y.-H.; Wong, H.-L.; Yam, V.W.-W. From Spherical to Leaf-Like Morphologies: Tunable  
390 Supramolecular Assembly of Alkynylgold(I) Complexes through Variations of the Alkyl Chain  
391 Length. *Chem. Eur. J.* **2015**, *21*, 5732-5735.
- 392 17. Lanoe, P.H.; Chan, J.; Gontard, G.; Monti, F.; Armaroli, N.; Barbieri, A.; Amouri, H. Deep-Red  
393 Phosphorescent Iridium(III) Complexes with Chromophoric N-Heterocyclic Carbene Ligands:  
394 Design, Photophysical Properties, and DFT Calculations. *Eur. J. Inorg. Chem.* **2016**, 1631-1634.

- 395 18. Nitsch, J.; Lacemon, F.; Lorbach, A.; Eichhorn, A.; Cisnetti, F.; Steffen, A. Cuprophilic interactions in  
396 highly luminescent dicopper(I)-NHC-picolyl complexes - fast phosphorescence or TADF? *Chem.*  
397 *Commun.* **2016**, *52*, 2932-2935.
- 398 19. Penney, A.A.; Sizov, V.V.; Grachova, E.V.; Krupenya, D.V.; Gurzhiy, V.V.; Starova, G.L.; Tunik,  
399 S.P. Auophilicity in Action: Fine-Tuning the Gold(I)-Gold(I) Distance in the Excited State To  
400 Modulate the Emission in a Series of Dinuclear Homoleptic Gold(I)-NHC Complexes. *Inorg. Chem.*  
401 **2016**, *55*, 4720-4732.
- 402 20. Diness, F.; Fairlie, D.P. Catalyst-Free N-Arylation Using Unactivated Fluorobenzenes. *Angew. Chem.*  
403 *Inter. Ed.* **2012**, *51*, 8012-8016.
- 404 21. Wang, H.M.J.; Lin, I.J.B. Facile synthesis of silver(I)-carbene complexes. Useful carbene transfer  
405 agents. *Organometallics* **1998**, *17*, 972-975.
- 406 22. Visbal, R.; Laguna, A.; Gimeno, M.C. Simple and efficient synthesis of [MCl(NHC)] (M = Au, Ag)  
407 complexes. *Chem. Commun.* **2013**, *49*, 5642-5644.
- 408 23. Gimeno, M.C.; Laguna, A.; Visbal, R. N-Heterocyclic Carbene Coinage Metal Complexes as Intense  
409 Blue-Green Emitters. *Organometallics* **2012**, *31*, 7146-7157.
- 410 24. Wang, H.A.J.; Vasam, C.S.; Tsai, T.Y.R.; Chen, S.H.; Chang, A.H.H.; Lin, I.J.B. Gold(I)  
411 N-heterocyclic carbene and carbazolate complexes. *Organometallics* **2005**, *24*, 486-493.
- 412 25. Alexiou, M.S.; Tychopoulos, V.; Ghorbanian, S.; Tyman, J.H.P.; Brown, R.G.; Brittain, P.I. The  
413 Uv-Visible Absorption and Fluorescence of Some Substituted 1,8-Naphthalimides and Naphthalic  
414 Anhydrides. *J. Chem. Soc., Perkin, Trans.* **1990**, 837-842.
- 415 26. Srivastava, A.K.; Singh, A.; Mishra, L. Tuning of Aggregation Enhanced Emission and Solid State  
416 Emission from 1,8-Naphthalimide Derivatives: Nanoaggregates, Spectra, and DFT Calculations.  
417 *Journal of Physical Chemistry A* **2016**, *120*, 4490-4504.
- 418 27. Brouwer, A.M. Standards for photoluminescence quantum yield measurements in solution (IUPAC  
419 Technical Report). *Pure Appl. Chem.* **2011**, *83*, 2213-2228.
- 420 28. Armarego, W.L.F.; Chai, C.L.L. Purification of Laboratory Chemicals Fifth Edition **2003**.
- 421 29. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.
- 422 30. Farrugia, L. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.*  
423 **1999**, *32*, 837-838.



424 1. © 2017 by the authors. Submitted for possible open access publication under the  
425 terms and conditions of the Creative Commons Attribution (CC BY) license  
426 (<http://creativecommons.org/licenses/by/4.0/>).

427

428