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

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**Abstract:** A series of novel *N*-heterocyclic carbene coinage metal complexes containing a naphthalimide (NI) chromophore has 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  $[(L^1)-M-X]$ ,  $M = Cu$ ,  $X = Cl$  (**1a**);  $M = Ag$ ,  $X = I$  (**1b**) and  $M = Au$ ,  $X = Cl$ , (**1c**). While in the second family, a  $\pi$ -extended carbene ligand precursor  $L^2-H^+I^-$  (**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  $[(L^2)-M-Cl]$ ,  $M = Cu$  (**2a**) and  $M = Au$  (**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  $Au \cdots Au$  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 the intraligand origin of the NI chromophore. Moreover, the carbene complexes featuring  $L^2$  ligand with  $\pi$ -extended system were found to be more luminescent.

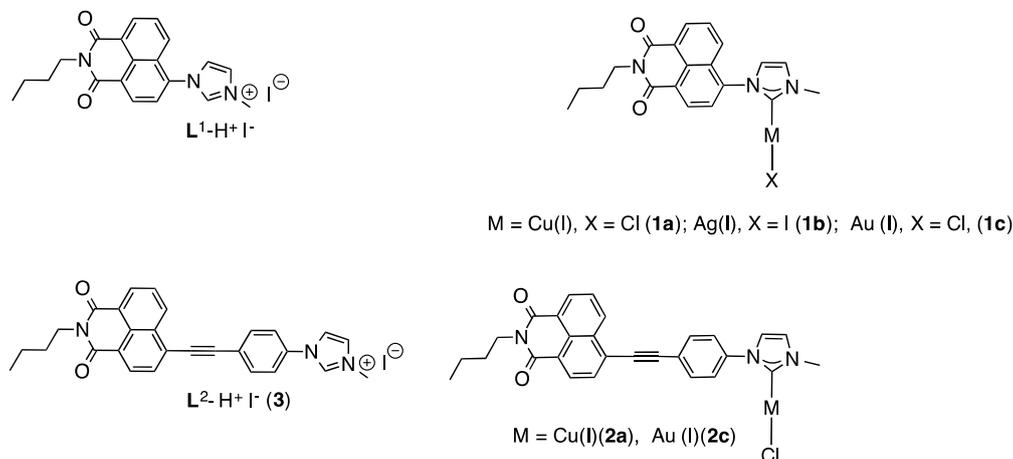
**Keywords:** *N*-heterocyclic carbenes; coinage metals; photophysical properties

## 1. Introduction

*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].

We recently reported the synthesis and characterization of a family of cyclometalated iridium carbene complexes containing a naphthalimide chromophore [17]. The latter behaved as deep red phosphorescent compounds with good quantum yields and long lifetimes. Thus we sought to extend our approach to other metal chromophores, mainly coinage metals. In fact, due to their linear geometry we expected them to promote metal–metal interactions [12,18,19] and hence add a novel property to this kind of compound relative to the cyclometalated iridium compounds. In this paper, we describe

the synthesis and photophysical properties of a novel class of *N*-heterocyclic carbene complexes of Cu(I), Ag(I) and Au(I) containing a naphthalimide chromophore. Two types of compounds are described: (i) those where the naphthalimide is directly linked to the carbene unit, while in the other case (ii) the organic chromophore is distant from the carbene unit via an alkyne arene linkage (Figure 1).

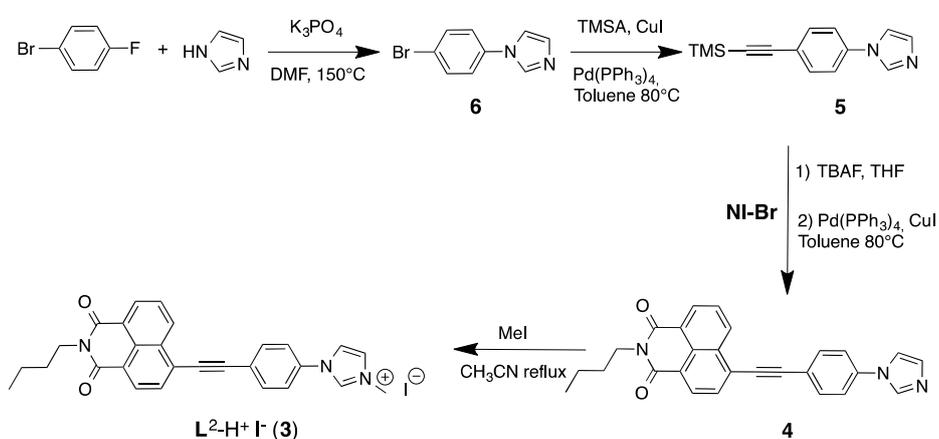


**Figure 1.** Ligand precursors  $L^1-H^+I^-$  and  $L^2-H^+I^-$  and the related NHC carbene complexes with naphthalimide chromophore described in this work.

## 2. Results and Discussions

### 2.1. Synthesis and Characterization of the Imidazolium Salts

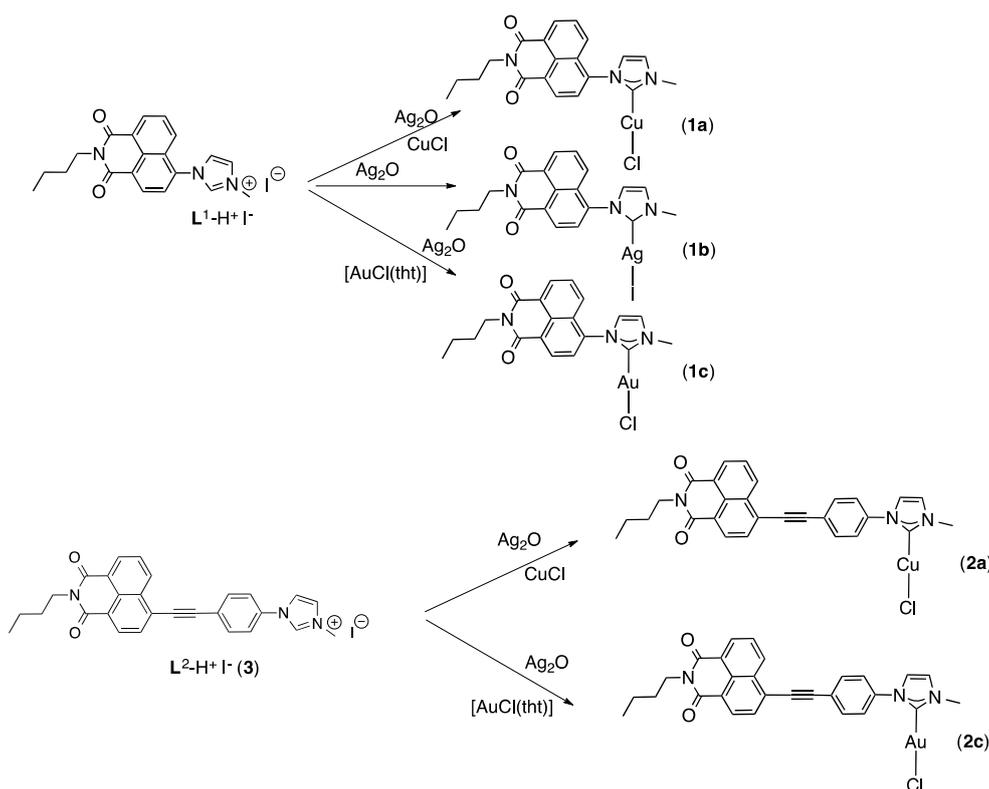
The carbene ligand precursor  $L^1-H^+I^-$  was prepared according to our previously reported procedure [17]. For  $L^2-H^+I^-$  containing an extended carbon skeleton, the product was prepared in several steps. Thus reaction of imidazole with *p*-bromofluorobenzene in the presence of potassium phosphate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



**Scheme 1.** Synthesis of the carbene ligand precursor  $L^2-H^+I^-$  (**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  $\text{Ag}_2\text{O}$  with  $\text{L}^1\text{-H}^+\text{I}^-$  in dry  $\text{CH}_2\text{Cl}_2$  solution and subsequent transmetalation with the appropriate metal sources (i.e.,  $\text{CuCl}$  or  $(\text{tht})\text{AuCl}$ ) leads to the formation of  $\text{Cu(I)}$  and  $\text{Au(I)}$  complexes in moderate to good yields [ $(\text{L}^1)\text{-Cu-Cl}$ ] (**1a**) (30%) [ $(\text{L}^1)\text{-Au-Cl}$ ] (**1c**) (72%). For comparison purposes, the silver complex was also prepared [ $(\text{L}^1)\text{-Ag-I}$ ] (**1b**) with a 94% yield (Scheme 2).



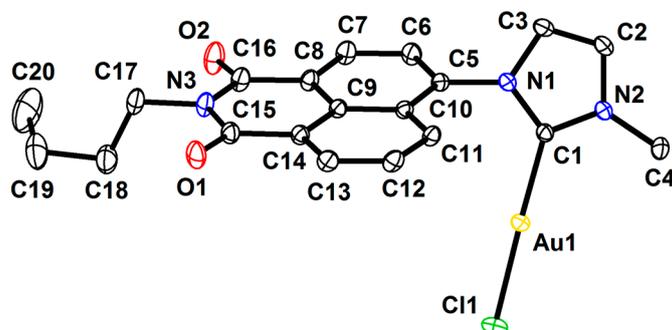
**Scheme 2.** Synthesis of the novel carbene coinage metal complexes.

On the other hand, we found that when using  $\text{L}^2\text{-H}^+\text{I}^-$  carbene precursor, the reactions were more tedious and required the use of a mixture of  $\text{CH}_3\text{NO}_2/\text{CH}_2\text{Cl}_2$  for solubility purposes. For instance, the [ $(\text{L}^2)\text{-Cu-Cl}$ ] (**2a**) and [ $(\text{L}^2)\text{-Au-Cl}$ ] (**2c**) were obtained at 33% and 72% yields respectively after 16 hours of reaction using  $\text{Ag}_2\text{O}$  precursor (Scheme 2). Despite all our efforts, we were unable to isolate the silver carbene complex [ $(\text{L}^2)\text{-Ag-I}$ ] (**2b**). All compounds have been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  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  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the azolium salts showed the presence of a singlet for the C–H group around  $\delta$  135 ppm while the related metal carbene complexes **1b**, **1c**, and **2c** displayed a singlet for the carbene carbon centers in the range of  $\delta$  171–182 ppm.

## 2.3. X-ray Molecular Structure of the N-heterocyclic Gold Carbene Complex [ $(\text{L}^1)\text{-Au-Cl}$ ] (**1c**)

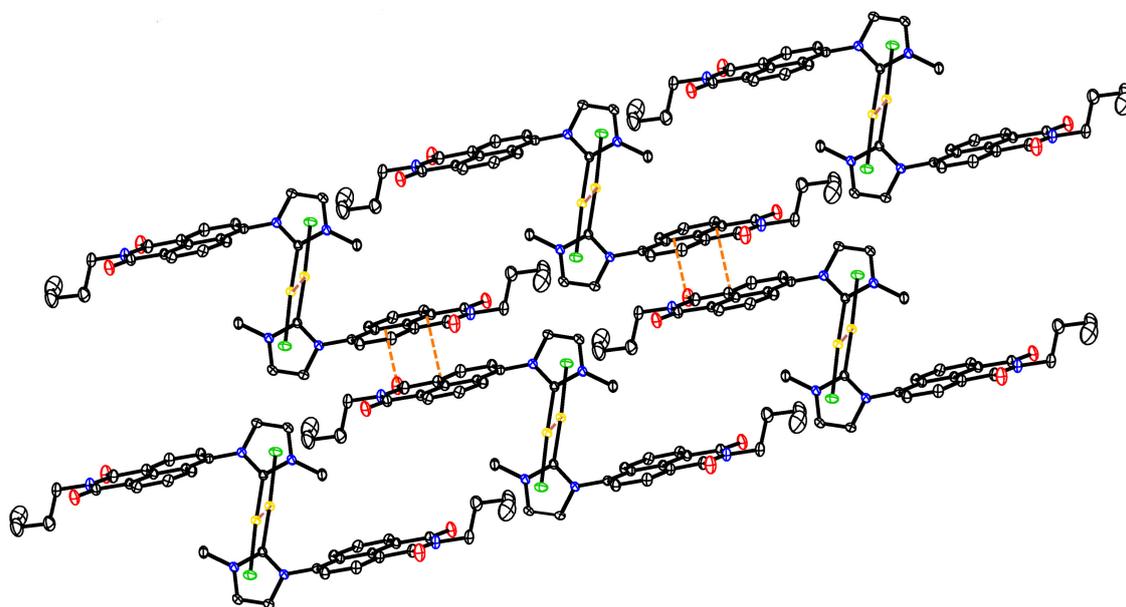
Convenient crystals for X-ray diffraction crystallography were grown by slow vapor diffusion of diethylether into a dichloromethane solution of [ $(\text{L}^1)\text{-Au-Cl}$ ] (**1c**) (Table S1). A view of the structure is given in Figure 2 with selected bond distances and angles. The structure confirms the formation of the target gold complex **1c**. Moreover, it shows the geometry around the  $\text{Au(I)}$  center is almost linear with a  $\text{C}_{\text{carbene}}\text{-Au-Cl}$  angle of approximately  $175.88(7)^\circ$ . The  $\text{C}_{\text{carbene}}\text{-Au}$  and  $\text{Au-Cl}$  distances are

1.985(5) Å and 2.287(0) Å, respectively, typical to those reported for previous complexes containing a simple carbene ligand [15,23,24]. In addition, the planes of the imidazole-2-ylidene moiety and the NI moiety show an angle of approximately of 65.81(8)°. To our knowledge, this is the first molecular structure of a gold carbene complex tethered to a naphthalimide chromophore.



**Figure 2.** View of the molecular structure of the gold carbene complex  $[(L^1)\text{-Au-Cl}]$  (**1c**). Selected bond distances (Å) and angle (°). Au(1)–C(1) = 1.986(2), Au(1)–Cl(1) = 2.287(1), N(1)–C(1) = 1.353(3), 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) = 1.457(3), C(1)–Au(1)–Cl(1) = 175.88(7), N(1)–C(1)–N(2) = 105.4(2).

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.

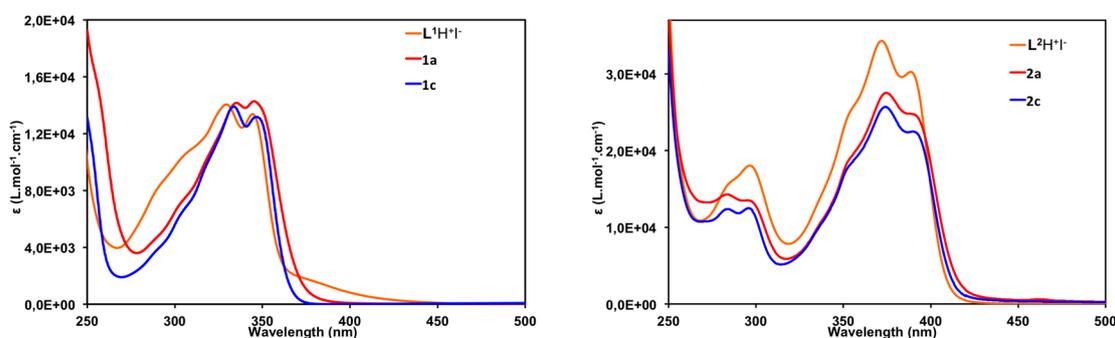


**Figure 3.** Crystal packing of **1c** showing aurophilic Au...Au contact at 3.407(1) Å between two individual molecules in head-to-tail fashion and  $\pi$ – $\pi$  interactions at 3.40 Å between two naphthalimide units to generate a 2D supramolecular structure.

#### 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  $[(L^1)\text{-Ag-I}]$  (**1b**), which was not stable in  $\text{CH}_2\text{Cl}_2$  solution and hence could not

be investigated. The imidazolium salts  $L^1-H^+I^-$  and  $L^2-H^+I^-$  display different absorption spectra. For instance, the  $L^2$  series are bathochromically shifted relative to  $L^1$  series due to  $\pi$ -conjugation (Figure 4). Moreover, they show additional absorption peaks at 280–320 nm, which are not present in the  $L^1$ -type ligand and related complexes. These bands are assigned to  $\pi \rightarrow \pi^*$  involving the acetylide unit (Figure 4). Furthermore the  $L^1-H^+I^-$  and the related carbene complexes  $[(L^1)-Cu-Cl]$  (**1a**) and  $[(L^1)-Au-Cl]$  (**1c**), show a broad absorption band between 300 nm and 400 nm with  $\epsilon$  values in the range of  $12.9 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  to  $14.2 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ , 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  $L^1-H^+I^-$  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  $L^1-H^+I^-$  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 systems [26].



**Figure 4.** Absorption spectra for the azolium salts of  $L^1-H^+I^-$ ,  $L^2-H^+I^-$  and the carbene metal complexes **1a–2a** and **1c–2c** in  $\text{CH}_2\text{Cl}_2$  solution at room temperature.

**Table 1.** Absorption and emission data for the azolium salts of  $L^1$  and  $L^2$ , and the carbene metal complexes **1a–2a** and **1c–2c** from  $\text{CH}_2\text{Cl}_2$  solutions at room temperature.

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

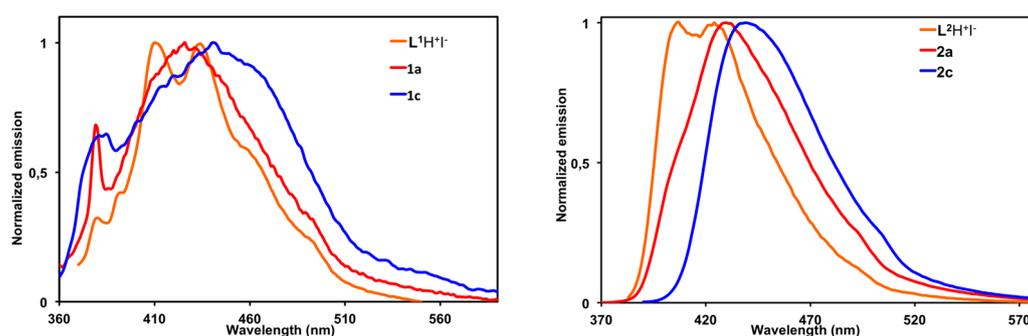
<sup>a</sup> Quantum yields (QYs) have been estimated by taking 9,10-diphenylanthracene in cyclohexane as a reference with QY = 0.90 [27]; <sup>b</sup>  $\lambda_{\text{max}}$ ; <sup>c</sup>  $\lambda_{\text{exc}} = 340 \text{ nm}$ ; <sup>d</sup>  $\lambda_{\text{exc}} = 350 \text{ nm}$ .

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

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

Preliminary results showed that the metal complexes **1a–2a** and **1c–2c** are luminescent at room temperature in  $\text{CH}_2\text{Cl}_2$  solution and displayed blue emissions (Figure 5) in the range of 420 to 451 nm (Table 1). For instance, the metal complexes containing  $L^1$ -type ligand showed a slight red shift emission relative to free to the azolium salt  $L^1-H^+I^-$  (Figure 4). Similarly, the carbene metal complexes with  $L^2$ -type ligand also showed a slight red shift relative to the free ligand  $L^2-H^+I^-$

(Figure 5). These emissions are clearly intraligand interactions centered at the naphthalimide moiety. Similar results were reported for coinage carbene complexes displaying organic chromophores [12,15,23].



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

On the other hand, we found that the complexes with  $L^2$ -type ligand displayed higher quantum yields (Table 1). Further studies at low temperature and in solid state will be conducted on these compounds in order to better understand their optical behavior.

### 2.5. Concluding Remarks

In this work, we reported the synthesis of the 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 [ $(L^1)-M-Cl$ ],  $M = Cu$  (**1a**),  $M = Ag$ , (**1b**) and  $M = Au$  (**1c**); while in the second series, the chromophore is moved away via an alkyne-arene linkage [ $(L^2)-M-Cl$ ],  $M = Cu$  (**2a**),  $M = Au$ , (**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 halogen groups to improve their quantum yields and seek applications as organic light emitting diodes.

## 3. Experimental Section

### 3.1. General Experimental Methods

Commercially available reagents were purchased from commercial suppliers and used as received unless otherwise specified. Solvents were obtained from same commercial sources and used without further purification unless otherwise specified.  $Et_3N$ ,  $CH_2Cl_2$ , and  $Et_2O$  were distilled respectively on sodium,  $CaH_2$ , and sodium/benzophenone. Toluene was stored over 4 Å molecular sieve under Ar. Copper(I) chloride has been prepared according to a reported procedure [28] and stored in a Schlenk tube under Ar. Glassware was oven-dried prior to use.  $^1H$  NMR spectra (were recorded on a Bruker (Karlsruhe, Germany) 300 MHz and on a 400 MHz spectrometer in  $CDCl_3$ ,  $CD_2Cl_2$  or  $(CD_3)_2SO$  and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ( $CDCl_3$  7.26 ppm,  $CD_2Cl_2$  5.32 ppm, and  $(CD_3)_2SO$  2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, or overlap of non-equivalent resonances), integration.  $^{13}C$  NMR spectra were recorded either on a 75.4 MHz or on a 101 MHz in  $CDCl_3$ ,  $CD_2Cl_2$ , or  $(CD_3)_2SO$  and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ( $CDCl_3$  77.16 ppm,  $CD_2Cl_2$  53.84 ppm, and  $(CD_3)_2SO$  39.52 ppm). Absorption measurement has been performed on a Jasco V-670

(JASCO International Co. Ltd., Tokyo, Japan) and luminescence measurement on a Jasco FP-8300 Fluorometer (JASCO International Co. Ltd., Tokyo, Japan).

### 3.2. Synthesis of Compound 5

In an oven-dried Schlenk tube under Ar atmosphere, 1-(4-Bromophenyl)-imidazole 6 (2 g, 8.97 mmol), CuI (51 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 Et<sub>3</sub>N (2 mL). The solution was degassed three times using freeze-pump-thaw technique. (TMSA = Trimethylsilylacetylene) (1 mL, 6.72 mmol) was added to the solution and heated at 80 °C overnight (16 h). The mixture was then heated at 50 °C and solvents were evaporated to dryness. At r.t., the dark crude material was treated with Et<sub>2</sub>O and the suspension was filtrated on Dicalite<sup>®</sup>. The solvent was evaporated and a column chromatography (SiO<sub>2</sub>, 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, 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} 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 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.

### 3.3. Synthesis of Compound 4

Tetrabutylammonium fluoride monohydrate (1.153 g, 4.41 mmol) was added to a solution of compound 5 (1 g, 4.16 mmol) in tetrahydrofuran (THF) (25 mL). The reaction was monitored by thin-layer chromatography (TLC) (SiO<sub>2</sub>, ethylacetate) and after full conversion, deionized water (20 mL) was added and the aqueous phase was extracted three times with Et<sub>2</sub>O. The combined organic layers were washed two times with brine, dried over MgSO<sub>4</sub>, and solvents were removed under reduce pressure. The crude product was engaged in the next step without further purification. In a dry Schlenk tube under Ar, the crude alkyne (603 mg, 3.59 mmol), 4-bromonaphthalimide (1.312 g, 3.95 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (126 mg, 0.18 mmol), and CuI (34 mg, 0.18 mmol) were dissolved/suspended in a mixture of toluene (20 mL) and 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 monitored by TLC (SiO<sub>2</sub>, ethylacetate/C<sub>6</sub>H<sub>12</sub>). After full conversion (roughly 2 h), the solvents were removed and the dark material was treated with CH<sub>2</sub>Cl<sub>2</sub>. The dark solution was filtrated on Dicalite<sup>®</sup> and the solvents were removed under reduced pressure. A chromatography column was performed (SiO<sub>2</sub>, from pure CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 7/3). The fractions containing the compound were combined and the solvent was removed under vacuum. The yellow solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed three times with a solution of K<sub>2</sub>CO<sub>3</sub> (1 N) and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the compound was obtained as yellow solid (1.175 g, 78%). <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* = 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 (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, *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, 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 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.

### 3.4. Synthesis of L<sup>2</sup>-H<sup>+</sup>I<sup>-</sup> (3)

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 the solution was refluxed overnight. The solvent was evaporated to dryness and the crude material was stirred 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 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), 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 (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* = 7.3 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO) δ 163.1, 162.8, 136.2, 135.1, 133.7, 131.9, 131.3, 130.8, 129.9, 128.4, 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  $C_{28}H_{24}IN_3O_2 \cdot 1/10Et_2O$ , C, 59.97; H, 4.43; N, 7.39; found C, 59.85; H, 4.18; N, 7.34.

### 3.5. Synthesis of Complex **1b**

An oven-dried Schlenk under Ar was loaded with  $L^1-H^+I^-$  (143 mg, 0.3 mmol) and  $Ag_2O$  (38 mg, 0.17 mmol) and the solids were suspended in a mixture of distilled  $CH_2Cl_2$  and  $CH_3CN$  (1/1, 20 mL). The solution was stirred for 4–5 h and protected from light using aluminum foil. Then a pinch of active carbon was added and the solution was filtered on Dicalite<sup>®</sup> and washed with a small amount of  $CH_2Cl_2$ . The solution was reduced under vacuum, subsequent addition of  $Et_2O$  provided a precipitate. The supernatant was filtered off with a cannula and the solid was dried under vacuum. **1b** was obtained as a green solid (96 mg, 94%).  $^1H$  NMR (400 MHz, 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), 1.65 (p,  $J = 7.5$  Hz, 2H), 1.38 (h,  $J = 7.3$  Hz, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H).  $^{13}C\{^1H\}$  NMR (101 MHz, DMSO)  $\delta$  182.8, 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 Calcd. for  $C_{20}H_{19}AgIN_3O_2 \cdot CH_2Cl_2$ : C, 38.62; H, 3.24; N, 6.43; found C, 38.64; H, 2.98; N, 6.63.

### 3.6. General Procedure for the Synthesis of **1a** and **1c**

An oven-dried Schlenk under Ar was loaded with the imidazolium salt (1 eq.) and  $Ag_2O$  (from 0.5 eq. to 0.56 eq.) and the solids were suspended in a mixture of  $CH_2Cl_2$  and  $CH_3CN$  (1/1). The solution was stirred for 4–5 h under light protection using aluminum foil. Then a pinch of active carbon was added and the solution was filtered with a cannula fitted with a filter paper and the black solid was washed with a small amount of  $CH_2Cl_2$ . The solution was reduced under vacuum subsequent addition of  $Et_2O$  provided a precipitate. The supernatant was filtrate off with a cannula fitted with a filter paper and the solid was dried under vacuum. The desired metal salt was then added to the crude Ag(I) complex in  $CH_2Cl_2$ . The solution was stirred overnight at r.t. The yellowish precipitate was filtered off with a cannula fitted with a filter paper. The solid was washed two times with  $CH_2Cl_2$  and the solution was concentrated under vacuum, subsequent addition of  $Et_2O$  provided the desired complex which was separated and dried.

### 3.7. For Complex **1a**

$L^1-H^+I^-$  (95 mg, 0.2 mmol),  $Ag_2O$  (26 mg, 0.11 mmol) and  $CH_2Cl_2/CH_3CN$  (14 mL).  $CuCl$  (20 mg, 0.2 mmol) and  $CH_2Cl_2$  (10 mL). The complex was obtained as an yellow solid (22 mg, 30%). Analysis calcd. for  $C_{20}H_{19}CuClN_3O_2 \cdot 1/4CH_2Cl_2$ : C, 53.62; H, 4.33; N, 9.26; found, C, 53.70; H, 4.57; N, 8.99.  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  8.77–8.64 (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 (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).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CD_2Cl_2$ )  $\delta$  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.

### 3.8. For Complex **1c**

$L^1-H^+I^-$  (95 mg, 0.2 mmol),  $Ag_2O$  (23 mg, 0.1 mmol) and  $CH_2Cl_2/CH_3CN$  (14 mL).  $(tth)AuCl$  (64 mg, 0.2 mmol) and  $CH_2Cl_2$  (10 mL). The complex was obtained as an off white solid (73 mg, 72%).  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  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), 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).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CD_2Cl_2$ )  $\delta$  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, 20.7, 14.0. Analysis calcd. for  $C_{20}H_{19}AuClN_3O_2 \cdot 1/4CH_2Cl_2$ : C, 41.43; H, 3.35; N, 7.43; found, C, 41.00; H, 3.17; N, 7.19.

### 3.9. General Procedure for the Synthesis of **2a** and **2c**

In an oven-dried Schlenk tube protected from light with aluminum foil, iodide salt, and Ag<sub>2</sub>O were suspended in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>NO<sub>2</sub> mixture (4/1, *v/v*). After 5–6 h, a yellow suspension was formed and the desired metal precursor (whether (tht)AuCl or CuCl) was added to the suspension. After 12–16 h of stirring, the solution was filtered off with a cannula and the filtrate was separated into a Schlenk tube as translucent yellow solution. The remaining solid was washed three times with CH<sub>2</sub>Cl<sub>2</sub> and the filtrate was concentrated under vacuum subsequent Et<sub>2</sub>O addition provided a precipitate, the mixture was then allowed to stand in a freezer for several hours. The supernatant was filtered off with a cannula fitted with a filter paper and the yellow solid was dried under vacuum.

#### 3.10. For Complex **2a**

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 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 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 (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 (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, 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, 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</sub>·4/10CH<sub>2</sub>Cl<sub>2</sub>: C, 60.22; H, 4.23; N, 11.22, found C, 60.13; H, 4.11; N, 7.81.

#### 3.11. For Complex **2c**

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 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 (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), 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, 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 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, 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, 6.31, found C, 50.09; H, 3.39; N, 6.35.

#### 3.12. X-ray Crystal Structure Determination

A single crystal of [(L<sup>1</sup>)-Au-Cl] (**1c**) was selected, mounted, and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system (Bruker AXS, Karlsruhe, Germany) using fine-focus sealed-tube radiation. Unit-cell parameters determination, data collection strategy, integration, and absorption correction were carried out with the Bruker APEX2 suite of programs (v2014.11-0, Bruker AXS, Karlsruhe, Germany). The structure was solved with SHELXT-2014 [29] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014 [29] using the WinGX suite [30]. Relevant data was deposited at the Cambridge Crystallographic Data Center with number CCDC 1558193 and can be obtained free of charge via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

#### 3.13. Crystal Data for (**1c**)

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 = 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 transmission = 0.36/0.84, θ range = 2.23° to 30.58°, 29802 reflections measured, 5978 independent (*R*<sub>int</sub> = 0.0187), 5540 observed [*I* > 2σ(*I*)], completeness = 0.996, 246 parameters, 0 restraints, final *R* indices *R*1 [*I* > 2σ(*I*)] = 0.0209 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>.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2304-6740/5/3/58/s1](http://www.mdpi.com/2304-6740/5/3/58/s1), Cif and cif-checked files. Table S1: crystallographic data for complex [(L<sup>1</sup>)-Au-Cl] (1c), Figure S1: Absorption spectrum of the azolium 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 the same concentration and at room temperature.

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