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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 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 [($\mathbf{L}^1$)-M-X], M = Cu, X = Cl (**1a**); M = Ag, X = I (**1b**) and M = Au, X= Cl, (**1c**). While in the second family a π-extended carbene ligand precursor $\mathbf{L}^2H^+ I^-$ (**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 [($\mathbf{L}^2$)-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----Au at 3.407Å 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 chromphore. Moreover the carbene complexes featuring L^2 ligand with π-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 to promote metal--metal interactions[12,18,19] and hence add a novel property to this kind of compounds 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).

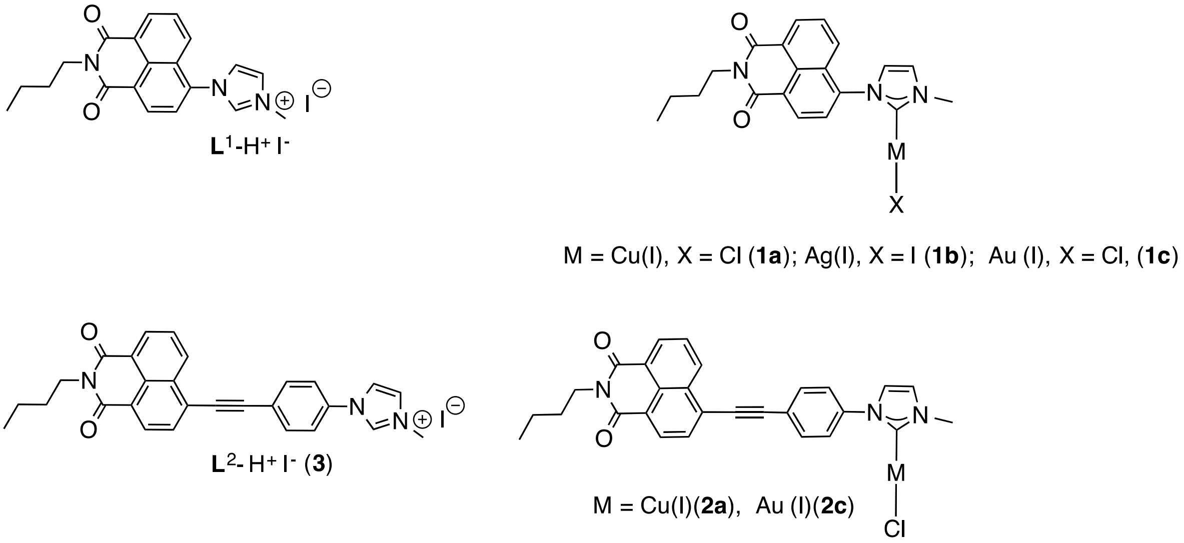
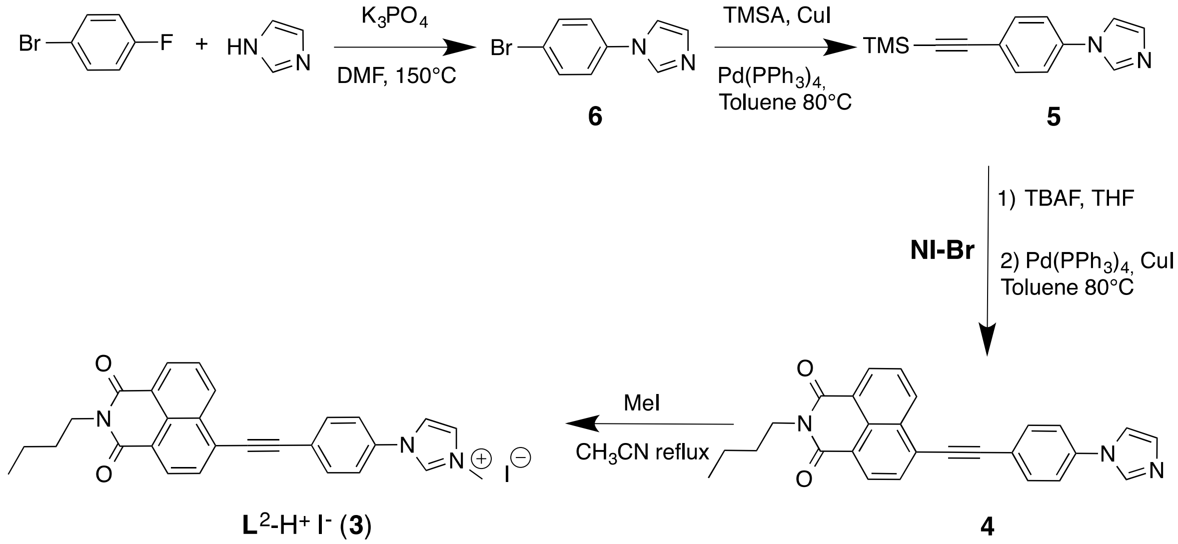


Figure 1. Ligand precursors **L**^{1}-H$^+$I$^-$ and **L**^{2}-H$^+$I$^-$ and the related NHC carbene complexes with naphthalimide chromophore described in this work.

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 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 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.

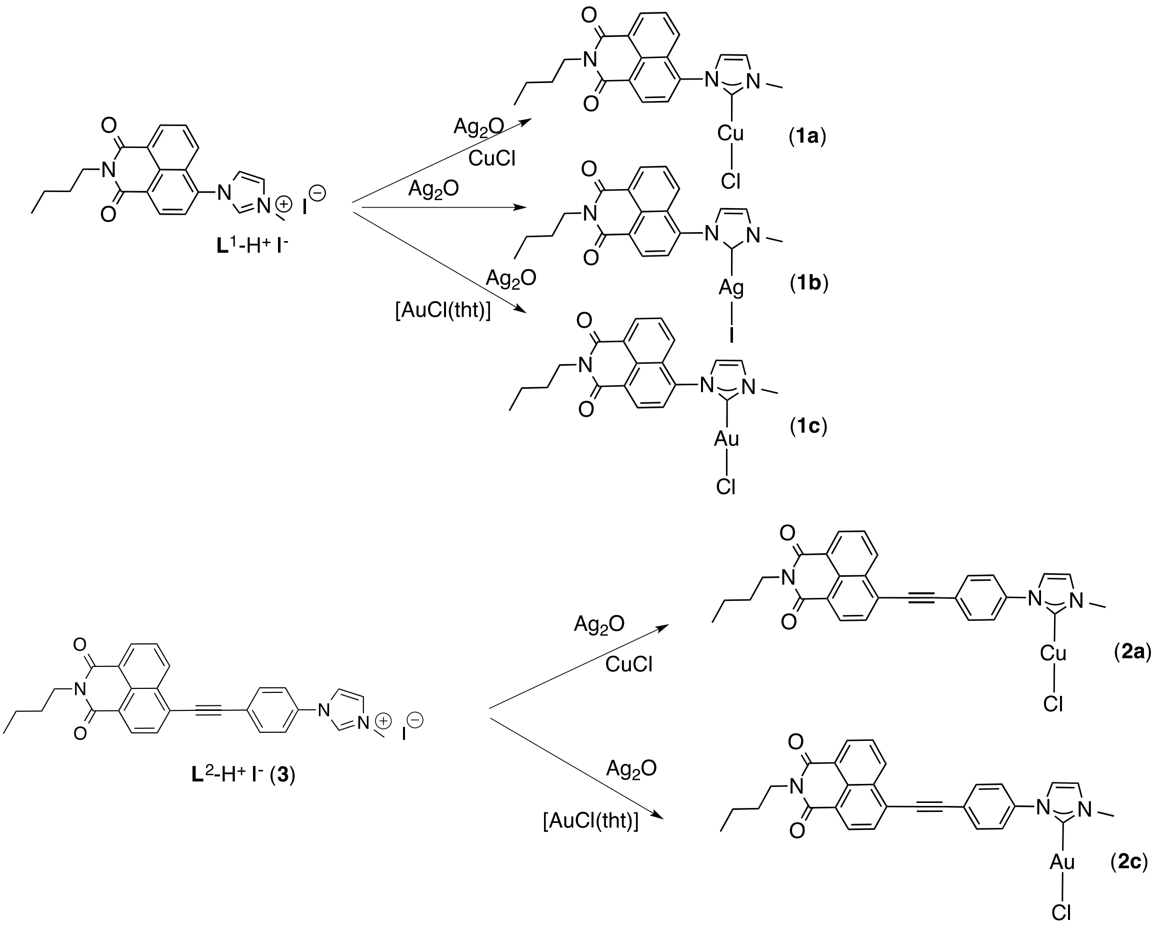


Scheme 1. Synthesis of the carbene ligand precursor **L**^{2}-H$^+$I$^-$ **(3)**.

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 Ag_2O with **L**^{1}-H$^+$ I$^-$ in dry CH_2Cl_2 solution and subsequent transmetallation with the appropriate metal sources (i.e. CuCl or (tht)AuCl leads to the formation of Cu(I) and Au(I) complexes in moderate to good yields [(**L**^{1})-Cu-Cl] (**1a**) (30%) [(**L**^{1})-Au-Cl] (**1c**) (72%). For comparison purposes the silver complex was also prepared [(**L**^{1})-Ag-I] (**1b**) in 94% yield.

On the other hand we found that using **L**^{2}-H$^+$I$^-$ carbene precursor the reactions were more tedious and required the use of a mixture of CH_3NO_2/CH_2Cl_2 for solubility purposes. For instance the [(**L**^{2})-Cu-Cl] (**2a**) and ([(**L**^{2})-Au-Cl] (**2c**) were obtained (33%) and (72%) yield respectively after 16 hours of reaction using Ag_2O precursor. Despite all our efforts we were unable to isolate the silver carbene complex [(**L**^{2})-Ag-I] (**2b**). All compounds have been characterized by ^1H and ^{13}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 $^{13}C\{^1H\}$ 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.



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

*2.3 X-ray molecular structure of the N-heterocyclic gold carbene complex [(L^1)-Au-Cl] (**1c**)*

Convenient crystals for X-ray diffraction crystallography were grown by slow vapor diffusion of diethylether into a dichloromethane solution of [(**L**^{1})-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 Au(I) center is almost linear with a $C_{carbene}$-Au-Cl angle of approximately 175.88(7)°. The $C_{carbene}$-Au and Au-Cl distances are 1.985(5) Å and 2.287(0), 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.

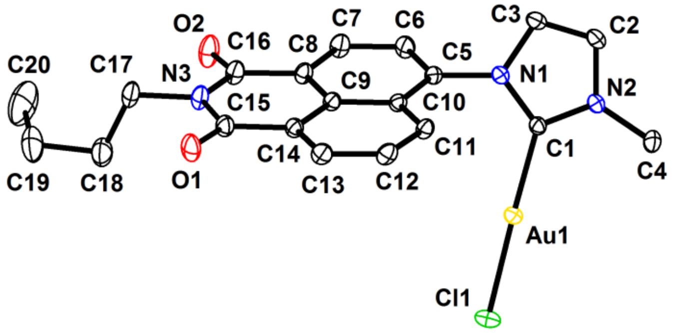


Figure 2. View of the molecular structure of the gold carbene complex [(**L**^{1})-Au-Cl] (**1c**). Selected bond distances (Å) and angle (°). Au(1)–C(1) = 1.986(2), Au(1)–Cl(1) = 2.287(1), N(1)–C(1) = 1.353(3), N(1)–C(3) = 1.388(3), N(1)–C(5) = 1.427(3), N(2)–C(1) = 1.338(3), N(2)–C(2) = 1.381(3), N(2)–C(4) = 1.457(3), C(1)–Au(1) –Cl(1) = 175.88(7), N(1)–C(1) –N(2) = 105.4(2).

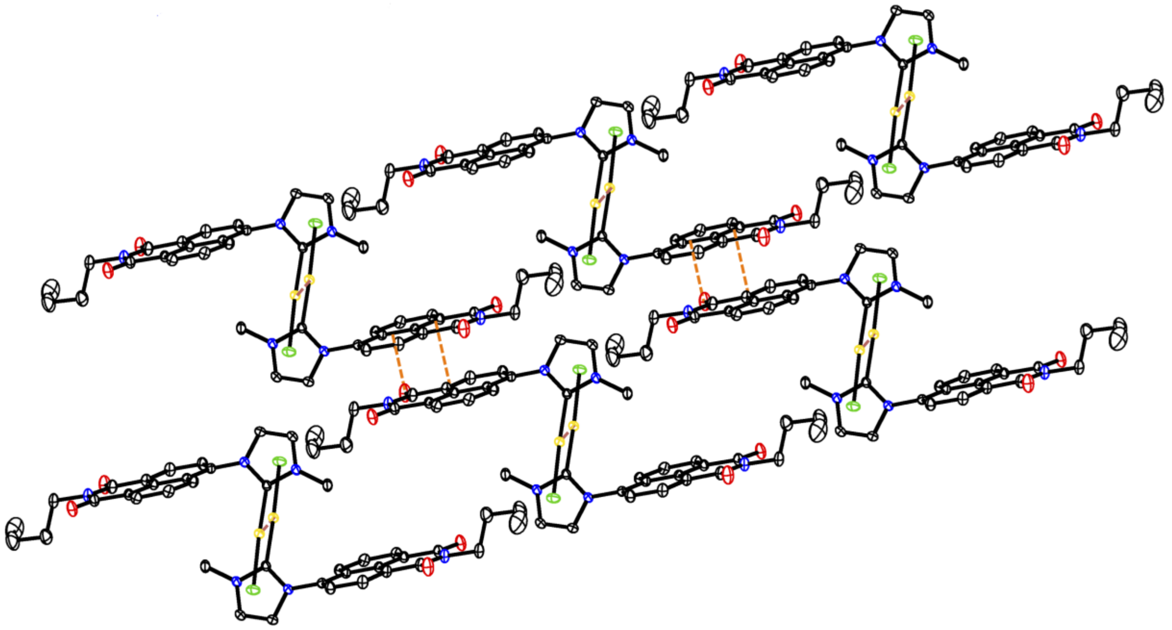


Figure 3. Crystal packing of **1c** showing aurophilic Au---Au contact at 3.407(1) Å between two individual molecules in head to tail fashion and π-π interactions at 3.40 Å between two naphthalimide units to generate a 2D supramolecular structure.

An examination of the crystal packing reveals that the individual molecules display Au---Au and π-π 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 π-π 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 CH_2Cl_2 solution except for silver carbene complex [(**L**^{1})-Ag-I] (**1b**) which was not stable in CH_2Cl_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 π-conjugation (Figure 3). More over 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 π→π* involving the acetylide unit (Figure 3). 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 (12.0 x 10^3 L.mol^{-1}.cm^{-1}<◎◎◎◎◎ <15.3 x 10^3 L.mol^{-1}.cm^{-1}), which might be a superposition of at least two bands, (Figure 4 and table 1). These bands might be attributed to ^{1}n→π* or π→π* transitions which are in agreement to those reported for the functionalized naphthalimide chromphore[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 CH_2Cl_2. Indeed we then recorded the UV visible spectrum of **L**^{1}-H$^+$ I at the same concentration but in CH_3CN 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 **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 320nm and 430nm and is red shifted compared to the previous compounds we also note that the molar absorptivity is higher.

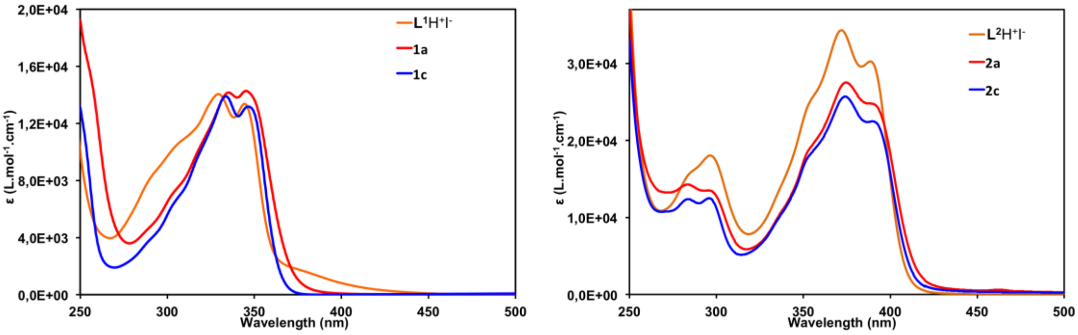


Figure 4. Absorption spectra for the azolium salts of **L**^{1}-H$^+$I$^-$, **L**^{2}-H$^+$I$^-$ and the carbene metal complexes **1a**-**2a** and **1c**-**2c** in CH$_2$Cl$_2$ solution at room temperature.

Both features can be explained by the extended π-conjugation as a result of the to 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 CH$_2$Cl$_2$ solution and displayed blue emissions 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 showed also a slight red shift relative to the free ligand **L**^{2}-H$^+$I. 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].

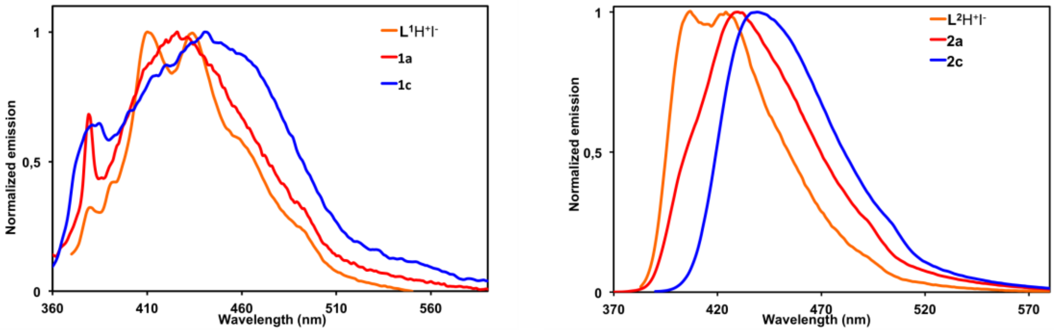


Figure 5. Normalized emission for the azolium salts of **L**^{1}-H$^+$I$^-$, **L**^{2}-H$^+$I$^-$ and the carbene metal complexes **1a**-**2a** and **1c**-**2c** in CH$_2$Cl$_2$ solution at room temperature.

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.

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

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 CH_2Cl_2 solutions at room temperature. a) Quantum yields (QYs) have been estimated by taking 9,10-diphenylanthracene in cyclohexane as a reference with QY = 0,90[27]. b) λ_{max} c) λ_{exc} = 340 nm. d) λ_{exc} = 350 nm.

2.5 Concluding remarks

In this work we reported the synthesis of first family of coinage metal complexes containing a choromophoric *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 π-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.

3. Experimental section

General experimental methods

Commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI Chemical, Strem or Fluorochem 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/benzophenon. 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. ^{1}H NMR spectra were recorded on a 300 MHz and on a 400 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 ($CDCl_3$ 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 and luminescence measurement on a Jasco FP-8300 Fluorometer.

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 $Pd(PPh_3)_2Cl_2$ (189 mg, 0.27 mmol) were introduced in a mixture of toluene (15 mL) and Et_3N (2 mL). The solution was degassed three times using freeze-pump-thaw technique. TMSA (1 mL, 6.72 mmol) was added to the solution and heated at 80 °C overnight (16h). 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_2O and the suspension was filtrated on Dicalite®. The solvent was evaporated and a column chromatography (SiO_2, ethylacetate/cyclohexane from 7/3 to 1/0) to give a greyish compound 5 (1.953 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) 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). $^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$) δ 137.1, 135.6, 133.7, 130.9, 122.6, 121.1, 118.0, 103.8, 96.0, 0.1. Analysis Calcd. for $C_{14}H_{16}N_2Si.1/10CH_2Cl_2$: C, 68.05; H, 6.56; N, 11.26; found C,68.48 ; H, 6.92; N, 11.09.

Synthesis of compound **4**

Tetrabutylamonium fluoride monohydrate (1.153 g, 4.41 mmol) was added to a solution of compound **5** (1 g, 4.16 mmol) in THF (25 mL). The reaction was monitored by TLC (SiO_2, ethylacetate) and after full conversion, deionized water (20 mL) was added and the aqueous phase was extracted three times with Et_2O. The combined organic layers were washed two times with brine, dried over $MgSO_4$ 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-bromonaphtalimide (1.312 g, 3.95 mmol), $Pd(PPh_3)_2Cl_2$ (126 mg, 0.18 mmol) and CuI (34 mg, 0.18 mmol) were dissolved/suspended in a mixture of toluene (20 mL) and Et_3N (2 mL). The solution was degassed three times. The mixture was then heated at 80 °C and the reaction was monitored by TLC (SiO_2, ethylacetate/C_6H_{12}). After full conversion (roughly 2hrs), the solvents were removed and the dark material was treated with CH_2Cl_2. The dark solution was filtrated on Dicalite® and the solvents were removed under reduce pressure. A chromatography column was performed (SiO_2, from pure CH_2Cl_2 to CH_2Cl_2/MeOH 7/3). The fractions containing the compound were combined and the solvent was removed under vacuum. The yellow solid was dissolved in CH_2Cl_2, washed 3 times with a solution of K_2CO_3 (1 N) and dried over $MgSO_4$. After evaporation of the solvent, the compound was obtained as yellow solid (1,175 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) 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). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) 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 $C_{27}H_{21}N_3O_2 .1/4H_2O$: C, 76.49; H, 5.11; N, 9.91; found C, 76.45; H, 5.04; N, 9.95.

Synthesis of $\mathbf{L}^{2}$-H^{+} I^{-} (**3**)

To a hot solution of 4 (156 mg, 0.37 mmol) in distilled CH_3CN (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_2O (40 mL). The solution was then filtered on a frit and the brown solid was wash three times with a small amount of Et_2O to give a brown solid (133 mg, 63 %). ^{1}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). ^{13}C{^{1}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 $C_{28}H_{24}IN_3O_2$.1/10Et_2O, C, 59.97; H, 4.43; N, 7.39; found C, 59.85; H, 4.18; N, 7.34.

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 during 4-5h and protected from light using aluminum foil. Then a pinch of active carbon was added and the solution was filtered on Dicalite® 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%). ^{1}H NMR (400 MHz, DMSO) δ 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{^{1}H} NMR (101 MHz, DMSO) δ 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 $C_{20}H_{19}AgIN_3O_2$ .CH_2Cl_2 C, 38.62 ; H, 3.24; N, 6.43; found C, 38.64; H, 2.98 ; N, 6.63.

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 4-5h 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 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.

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 $C_{20}H_{19}CuClN_3O_2$ .1/4CH_2Cl_2: C, 53.62; H, 4.33; N, 9.26; found, C, 53.70; H, 4.57; N, 8.99. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 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{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 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.

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). (tht)AuCl (64 mg, 0.2 mmol) and CH_2Cl_2 (10 mL). The complex was obtained as an off white solid (73 mg, 72%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 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{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 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 $C_{20}H_{19}AuClN_3O_2$ .1/4CH_2Cl_2: C, 41.43 ; H, 3.35 ; N, 7.43 ; found, C, 41.00; H, 3.17; N, 7.19.

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_2O were suspended in CH_2Cl_2/CH_3NO_2 mixture (4/1, v/v). After 5-6h, a yellow suspension was formed and the desired metal precursor (whether (tht)AuCl or CuCl) was added to the suspension. After 12-16h 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_2Cl_2 and the filtrate was concentrated under vacuum subsequent Et_2O 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.

For Complex **2a**

L^2-H$^+$I$^-$ (84 mg, 0.15 mmol), Ag$_2$O (19 mg, 0.08 mmol), CuCl (15 mg, 0.15 mmol) , CH$_2$Cl$_2$ (25 mL) and MeNO$_2$ (5 mL). The complex was obtained as a yellow solid (53 mg, 63%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) 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). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$) 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 $C_{28}H_{23}ClCuN_3O_2.4/10CH_2Cl_2$: C, 60.22; H, 4.23; N, 11.22, found C, 60.13; H, 4.11; N, 7.81.

For Complex **2c**

L^2-H$^+$I$^-$ (102 mg, 0.18 mmol), Ag$_2$O (23 mg, 0.10 mmol), (tht)AuCl (58 mg, 0,18 mmol), CH$_2$Cl$_2$ (25 mL) and MeNO$_2$ (5 mL). The complex was obtained as a yellow solid (38 mg, 33%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) 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). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$) 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 $C_{28}H_{23}ClAuN_3O_2$: C, 50.50; H, 3.48; N, 6.31, found C, 50.09; H, 3.39; N, 6.35.

X-Ray crystal structure determination.

A single crystal of [(**L**^{1})-Au-Cl] (**1c**) was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system 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. The structure was solved with SHELXT-2014[C1] 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 Centre with number CCDC 1558193 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Crystal data for (**1c**).

yellow prism, $C_{20}H_{19}N_3O_2ClAu$, 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^3, Z = 2, T= 200(1) K, λ = 0.71073 Å, μ = 7.663 mm^{-1}, min / max transmission = 0.36 / 0.84, θ range = 2.23° to 30.58°, 29802 reflections measured, 5978 independent (R_{int} = 0.0187), 5540 observed [$I>2\sigma(I)$], completeness = 0.996, 246 parameters, 0 restraints, final R indices R1 [$I>2\sigma(I)$] = 0.0209 and wR2 (all data) = 0.0520, GOF on F^2 = 1.089, largest difference peak / hole = 2.07 / -0.59 e.Å^{-3}.

Supplementary Materials: The following are available online at www.mdpi.com/link, Table S1: crystallographic data for complex [(**L**^{1})-Au-Cl] (**1c**), Figure S1: Absorption spectrum of the azolium salt **L**^{1}-H$^+$ I$^-$ in CH$_3$CN versus CH$_2$Cl$_2$ solution at same concentration and at room temperature.

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