N-Heterocyclic carbene metal complexes: Photoluminescence and applications

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N-Heterocyclic carbene metal complexes: Photoluminescence and applications

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This review covers the advances made in the synthesis of luminescent transition metal complexes containing *N*-heterocyclic carbene (NHC) ligands. The presence of a high field strength ligand such as an NHC in the complexes gives rise to high energy emissions, and consequently, to the desired blue colour needed for OLED applications. Furthermore, the great versatility of NHC ligands for structural modifications, together with the use of other ancillary ligands in the complex, provides numerous possibilities for the synthesis of phosphorescent materials, with emission colours over the entire visible spectra and potential future application in fields such as photochemical water-splitting, chemosensors, dye-sensitised solar cells, oxygen sensors, or medicine.

Introduction

The synthesis and characterisation of new *N*-heterocyclic carbene (NHC) transition metal complexes has undergone rapid development in the past two decades, and their application in medicine[1] and in a wide variety of catalytic processes[2] has been fascinating. However, luminescence is currently a "*hot topic*", and the potential that transition metal complexes containing NHC ligands have within this field is also of great importance.[3] Many optically active metal complexes bearing NHC ligands have been reported and some of them even patented because of the current interest in the preparation of new optical devices and organic light emitting diodes (OLEDs). The increasing use of the NHCs in a wide variety of applications arises from the great versatility of these ligands (Fig. 1). The unique electronic and steric properties can easily be modified by functionalisation of the imidazolium ring, principally at the nitrogen, with different organic and inorganic functions.

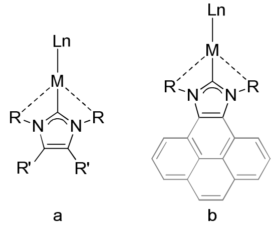


Fig. 1 Modification of electronic and bonding properties in M-NHC complexes.

The functionalisation of the NHC ligand can be utilised in different ways depending on the transition metal to which it is coordinated, and sometimes also on the oxidation state of this metal. Thus, for most middle-group transition metal complexes (groups 7-10) the presence of a chelating aromatic group such as a pyridine or even a phenyl group is desirable since they are capable of forming luminescent M-cyclometallated derivatives. Organometallic complexes of group 11 usually require the presence of either a chromophore group or a group which promotes the formation of dimeric or polymeric species by means of metallophilic interactions to impart the desired luminescence, with lifetimes corresponding to a fluorescence or phosphorescence process depending on the origin of the emissions. By changing the substituents or by a simple increase of the aromaticity in the backbone of the carbene motif it is possible to change the electronic properties and in this way to obtain suitable characteristics for their use as electron-rich groups. As previously mentioned, although there are many emissive M-NHC complexes, there are few reviews in which the luminescence of these species is discussed, the only examples focussing mainly on silver and gold complexes.[4] Here, we aim at compiling a thorough review of the luminescent *N*-heterocyclic carbene transition metal complexes reported to date, covering derivatives of transition metals from groups 7 to 11.

In the last few years, many luminescent transition metal complexes have been synthesised for use as luminophores in OLEDs. These materials have many applications such as flat panel displays and solid state lighting sources.[5-6] For such applications three-color white OLEDs are needed to generate a satisfying colour-rendering index (CRI). This is possible by the use of highly efficient deep blue, green and red phosphors with high quantum yields and very short luminescence decays (<5 μs). Organic light emitters usually only show fluorescence, and if triplet excitons are formed, they are deactivated by thermal processes. However, in transition metal complexes the strong spin-orbit coupling allows fast energy transfer from the singlet to the triplet state to occur. An electroluminescent device will form 25% singlet and 75% triplet excitons, hence the internal efficiency of an OLED can be improved by a factor of 4 when doped with a heavy-metal compound, giving efficiencies of up to 100%. Many efforts have focussed on improving the external quantum efficiency of such devices, mainly in the case of blue OLEDs, where achieving a deep blue colour and higher external quantum efficiencies is more difficult than for green or red OLEDs. The majority of OLED devices contain organic molecules doped with phosphorescent iridium or platinum derivatives. Another promising application for which ruthenium derivatives have been deeply studied is dye-sensitised solar cells (DSSCs). The essential requirement for a DSSC of high efficiency is a dye with a high energy LUMO level and a low energy HOMO level, and several approaches have been reported in which the HOMO energy level in this type of complex has been lowered.

Furthermore, it is likely that NHC complexes may have potential for many further applications, since similar phosphorescent transition metal complexes which do not contain NHC ligands are suitable in applications such as biological labelling agents (mainly rhenium and ruthenium derivatives),[7-9] charge-transfer reactions in DNA,[10] antitumoral agents (gold and platinum complexes),[11-12] phosphorescent sensors,[13] photocatalysis for CO_2 reduction[14] and photochemical water splitting.[15-16]

Luminescent M-NHC complexes and applications

In this review, luminescent M-NHC complexes are presented moving from the early-group to the late-group transition metals. Although many group 1-6 M-NHC complexes are known, to the best of our knowledge none of them have been described as luminescent. The first example of an emissive species is found in group 7.

Group 7: Rhenium

Many group 7 NHC metal complexes have been described, especially for Mn and Re.[17] However, only a few reports of luminescent rhenium(I) NHC complexes are found in the literature and the first example of an emissive Re(I)-NHC complex was reported by Che and coworkers.[18] It was found that by replacing the CO ligands with different diimine ligands, affording **1**, it was possible to modify the emission lifetimes or quantum yields by a simple variation in the electron withdrawing character of the R group (Fig. 2). Thus, the 4,4'-substituents on the bipyridine (bpy) strongly affected the metal to ligand charge transfer (MLCT) excited-state energy. The MLCT state energy could be modified by the polarity of the solvent, while the IL state energy remained unaffected by the solvent at room temperature.

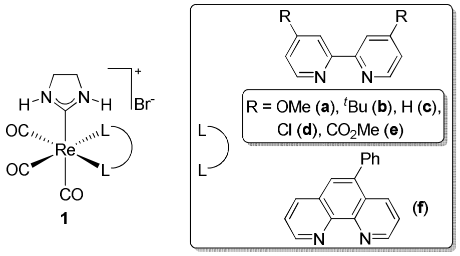


Fig. 2 First example of Re(I)-NHC complexes reported.

The second report of emissive Re(I)-NHC complexes came in 2011 with the complexes **2**, reported by Brown and coworkers (Fig. 3).[19] In this study, both complexes showed emission bands at around 500 nm but the analysis of the time resolved data revealed some significant differences in their photophysical behaviour. When both complexes were passed from air-equilibrated to degassed solutions, the chloride derivative (**2a**) showed an increase in both the luminescent lifetime and quantum yield, while the bromide derivative (**2b**) was found to be insensitive to the presence of O_2. It was proposed that this behaviour could be a result of the greater lability of the bromide ligand, and this idea was evidenced when acetonitrile, a more polar and coordinating solvent, was used for the emission studies. A red-shifted band was found and this was thought to arise from the solvent-assisted displacement of the bromide from the *fac*-$[Re(CO)_3(NHC)Br]$.

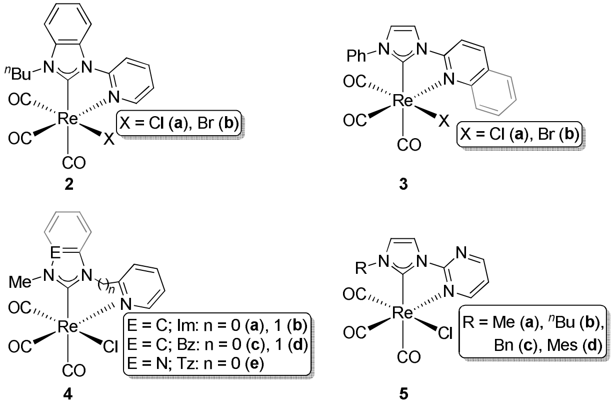


Fig. 3 Re(I)-NHC complexes reported recently.

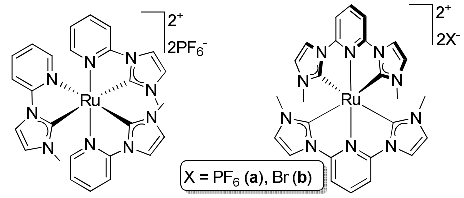
Very recently, the latter results were corroborated by the same research group.[20] Analogous complexes (**3**) with pyridine and quinoline type ligands were prepared, and after irradiation at 365 nm for 4 hours, a change in the emission profiles over time was observed (Fig. 3). This was characterised by the disappearance of an emission band at around 520 nm and the concomitant appearance of another band at around 590 nm for both chloro (**3a**) and bromo (**3b**) complexes derived from pyridine. In acetonitrile, photolysis of a carbonyl group *trans* to the NHC ligand was observed. For the quinoline derivatives no evidence of this behaviour was observed.

Carbene ligands derived from the imidazole (Im), benzimidazole (Bz) and triazole (Tz) were used by Chen and coworkers to prepare rhenium(I) complexes **4**.[21] Complexes functionalised with the 2-picolyl (**4b** and **4d**) were practically non-emissive, while complexes derived from the 2-pyridine (**4a** and **4c**) showed emissions in both the solid state and solution. The authors attributed this behaviour to the almost coplanar structure of the Re(I)-NHC complexes bearing the pyridyl group, thus allowing formation of a five-membered chelating ring. The presence of a methylene bridge between imidazole or benzimidazole and pyridine led to a more flexible structure, forming a six-membered ring and consequently resulting in a decrease of the luminescence. Furthermore, the differences found between the emission bands in the solid state and solution suggested a rigidochromic effect (an especially pronounced hypsochromic shift of the luminescence bands when the environment becomes more rigid), and an increase in the emission wavelengths in the order Tz > Im > Bz could be associated to the different electronic donor capacities of the

NHCs. Recently, with the aim of further tuning the luminescent properties of Re(I)-NHC complexes, Zheng and coworkers[22] reported the synthesis of some pyrimidine-functionalised NHC complexes, comparing the influence of the substituents in the carbene ligand, **5** (Fig. 3). The authors attributed the red shift found for the methyl (Me) derivative **5a** compared to its pyridine analogue (**4a**) to the more electron-deficient character of the pyrimidyl group compared to the pyridyl group. It was also found that variation of the substituent by benzyl (Bn), *n*-butyl (^{n}Bu) or mesityl (Mes) did not significantly affect the emissions or the luminescence quantum yields.

Group 8: Ruthenium and Osmium

As expected for derivatives with ferromagnetic properties, none of the reported *N*-heterocyclic carbene iron complexes have been described as emissive. However, since many luminescent bipyridine (bpy) and terpyridine (tpy) osmium and ruthenium complexes have been described, the preparation of analogous NHC complexes has been attempted, especially with the latter. The first photoluminescent study of such complexes bearing carbene ligands was reported by Chung and coworkers (Fig. 4).[23] It was found that **6**, which is an analogue of $Ru(bpy)_3^{2+}$, was non-emissive in acetonitrile at room temperature.



6 **7**

Fig. 4 Ru(II)-NHC complexes reported by Chung and coworkers.

Complex **7a,** however, showed a very strong emission at 532 nm with a long lifetime of 820 ns, 3820 times longer than the analogous $Ru(tpy)_2^{2+}$. Measurements of **7b** in water revealed an unexpected increase of the emission lifetime, reaching values up to 3100 ns, which was the longest among the reported luminescent lifetimes of the $Ru(tpy)_2^{2+}$ derivatives.

Several luminescent tetracyanoruthenate(II) complexes bearing NHC ligands have been prepared by Yam and coworkers (Fig. 5).[24] The energy absorption bands of complexes **8** and **9** were assigned mainly to intraligand (IL) transitions with some mixing of a $\pi(im)\rightarrow\pi^*(py)$ intraligand charge-transfer (ILCT) transition. A substantial change was observed for the low-energy band by the addition of acid to methanolic solutions. With these results and the sensitivity to substituent effects on the pyridine ring, the authors assigned the low-energy bands as a MLCT transition.

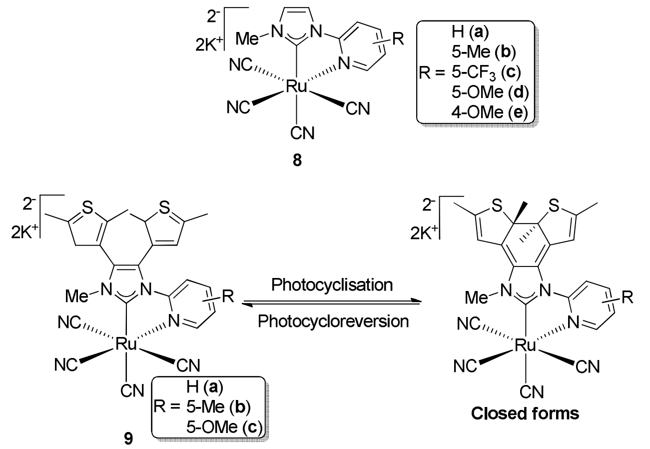
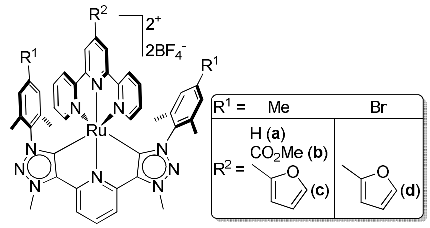


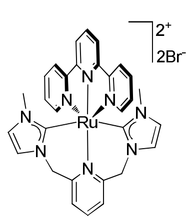
Fig. 5 Luminescent tetracyanoruthenates(II)-NHC complexes.

Upon excitation into either the IL or MLCT absorption band, all complexes (**8** and **9**) showed emission bands at around 500-600 nm with lifetimes between 0.5-2 μs, which follows a similar trend to that observed in the MLCT absorption band. Thus, the energy of the emissions was tentatively assigned as a ^{3}MLCT transition. It was also found that irradiation with an energy equivalent to that of the IL or MLCT absorption bands led complexes **9** to undergo a photocyclisation, generating the closed form of the complexes, which have a characteristic low-energy absorption band at around 500 nm and a shorter excited-state lifetime because of the presence of the photochromic moiety. This process was found to be reversible, and upon irradiation into the lowest-energy bands of the closed form species, photocycloreversion took place, recovering the open form of the complexes **9**.

Heteroleptic species (**10**) containing the classical tpy and an abnormal NHC ligand derived from 1,2,3-triazole were reported by Schubert and coworkers (Fig. 6). The superior σ-donation provided by the 1,2,3-triazolylidene in complex **10a** was found to lead to the destabilisation of the metal-centred triplet (^{3}MC) state, maintaining the MLCT character. The room-temperature luminescence measurements revealed an emission band at around 640 nm with an excited-state lifetime of 633 ns, which is 2500 times longer than that of $[Ru(tpy)_2](PF_6)_2$.[25] In further work, analogous ruthenium(II) complexes (**10a-10d**) were prepared with different substituents at the tpy ligand.[26] Again, the electronic absorption spectra of all complexes exhibited the typical absorption around 470 nm, along with red-emissions centred between 643 and 694 nm. Interestingly, these complexes showed unusually high emission lifetime values, especially complexes **10c** and **10d**, with τ = 6980 and 7900 ns, respectively, which are the highest reported lifetimes for unimolecular Ru(II) complexes. The authors suggested that the longer τ values of **10c** and **10d** relative to **10a** are associated to the increased separation between the emitting ^{3}MLCT state and the deactivating ^{3}MC state.



10

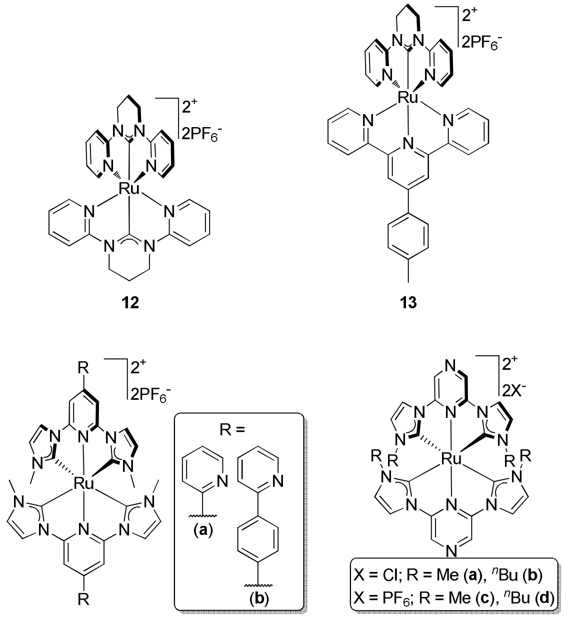


11

Fig. 6 Heteroleptic Ru(II) complexes bearing tpy and NHC ligands.

Similarly, Loiseau and coworkers prepared an analogous complex containing a classical NHC derived from imidazole, **11**.[27] They found this derivative to be emissive in acetonitrile both at room temperature and at 77 K, at 700 and 680 nm, respectively. These values were in good agreement with those found for $Ru(tpy)_2^{2+}$ derivatives, and again, the authors suggested a MLCT transition as the origin of these emissions.

Many attempts have been made to increase the ^{3}MLCT-^{3}MC gap and hence lengthen excited-state lifetimes. Schaper and coworkers compared the electrochemical and optical properties of homo- and heteroleptic ruthenium(II) complexes, **12** and **13** (Fig. 7).[28] In their study they confirmed that the NHC ligand has a stronger σ-ability than the tpy ligand, and this causes an increase in the energy gap between the ^{3}MLCT and ^{3}MC by destabilising the ^{3}MC. They also found a pronounced red-shift for the emissions of complexes **12** (753 nm) and **13** (735 nm) in the solid state, compared to the tpy analogue.

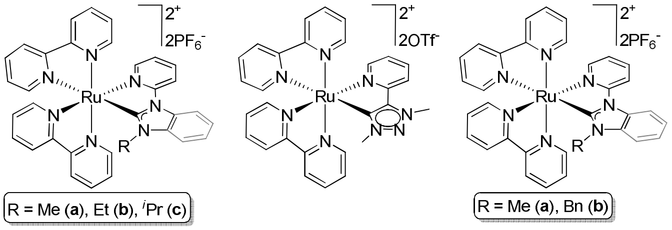


12 **13** **14** **15**

Fig. 7 Luminescent ruthenium(II)-NHC tpy-type complexes.

Other studies have focussed on the behaviour of the optical properties using different substituents on the 4′-position of a central pyridyl group or on the nitrogen atom of the carbenic ring. Chung and coworkers prepared homoleptic Ru(II) complexes (**14**) and analogous tpy derivatives (Fig. 7).[29] Absorption and luminescence spectra of complexes **14** showed a large blue-shift in the emission maxima (598 and 584 nm) compared with tpy derivatives (629 and 622 nm), and the excited-state lifetimes of all complexes exhibited bi-exponential decays with short components (0.8-13 ns). The principal characteristics exhibited by these complexes were the proton-dependent absorption and luminescent properties. The absorption spectra changed upon variation of the pH of the solution as a consequence of the free pyridyl group in each of the complexes, with a displacement of the absorption band and also a variation in the intensity of the signal. In a related study, Hwang and coworkers synthesised homoleptic Ru(II) complexes with a pincer NHC-pyrazine-NHC ligand (**15**), in which pyrazine is employed as a bridge between two NHCs (Fig. 7).[30] In this case, the absorption spectra for complexes **15** remained almost unaltered, indicating that the *N*-substituents and the anions of the complexes have minimal effect on the electronic structure. Again, a remarkable change in the absorption and emission spectra was observed upon addition of a strong acid. They not only found a red-shift in the absorption bands but also a dramatic decrease of the emission bands around 577 nm. The authors suggested the presence of a more efficient nonradiative decay as a consequence of the shift of the ^{3}MLCT state.

Recently, two research groups have been working on the study of photo- and electrochemiluminescent (ECL) properties of the Ru(II)-bpy complexes containing either a pyridine-functionalised imidazolylidene, benzimidazolylidene or triazolylidene NHC ligand (Fig. 8). Albrecht and coworkers found that complexes **16** and **17** showed similar electronic absorption bands to those of the $[Ru(bpy)_3]^{2+}$ derivative, which were attributed to ligand-centred (LC) π-π* (<300 nm) and to MLCT (410-470 nm) transitions.[31] Luminescence studies revealed that all complexes (**16** and **17**) were emissive upon excitation at 355 nm at room temperature in acetonitrile, with emission maxima around 615 nm. Furthermore, the excited-state lifetimes were found to be shorter than that of $[Ru(bpy)_3]^{2+}$. Complex **17** featured the smallest energy gap between the HOMO and LUMO orbitals (2.41 eV), which is expected to be beneficial for photovoltaic applications.



16 **17** **18**

Fig. 8 Ru(II)-bpy complexes containing NHC ligands.

At the same time, Barnard and coworkers demonstrated that the use of either NHC ligand (imidazolylidene or benzimidazolylidene) does not have a significant effect on the luminescent and ECL properties of complexes **18** (Fig. 8).[32] In their study, they observed that all complexes displayed intense to moderately intense ECL, highlighting the complex bearing the *N*-methyl-imidazol-based ligand, which produced ECL intensity of a slightly lower magnitude to the benchmark ECL emitter, $[Ru(bpy)_3]^{2+}$.

Many ruthenium(II) polypyridine complexes have been used as sensitisers for DSSCs, which are widely studied for renewable energy technologies.[33] Chung and coworkers have focussed their efforts on synthesising different symmetrical (**19**) and unsymmetrical (**20**) Ru(II) complexes bearing NHC/pyridine-based ligands and/or tpy ligands for application as photosensitisers in DSSCs (Fig. 9).[34] The overall efficiencies (η) of complexes **19** and **20** were found to be between 0.48-0.10%, significantly smaller than that of the di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) dye (6.34%), which has been considered as a standard reference for many DSSC systems. The authors attributed these results to the low short-circuit photocurrent density (J_{SC}) values with minor contributions from the open-circuit voltage (V_{OC}) and fill factors (FFs) of the complexes.

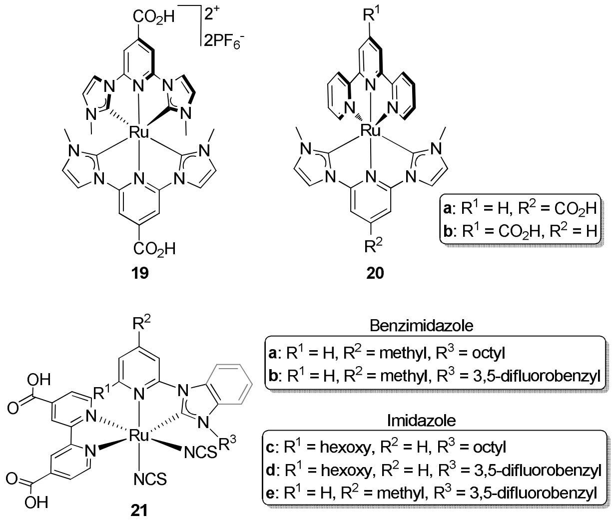


Fig. 9 NHC/pyridine-based ruthenium(II) complexes as DSSC sensitisers.

A short time later, Li and coworkers reported two photosensitisers, **21a** and **21b**, functionalised with electronically unsymmetrical benzimidazole/pyridine-based carbene ligands, which exhibited high *η* values (Fig. 9).[35] The UV-Vis studies revealed that the maximum absorptions were dependent on the solvent used, featuring two absorption bands around 450 and 540 nm and a distinct shoulder at around 630 nm extending to 750 nm, assigned as MLCT transitions. Both photosensitisers displayed higher cell efficiencies (9.69 and 9.04%) than that of N719-sensitised (8.98%), which represents an 8% over the N719 system for the complex with R^3 = octyl. In this case, the authors attributed these unexpected results to the presence of the NHC ligand, which promoted the high values of J_{SC} in the performances of DSSCs. In a further complementary study, the same group synthesised analogous complexes derived from imidazole/pyridine-based ligands (**21c**-**21e**).[36] Although the *η* values were lower than that of N719 sensitiser, the authors found that modification by replacing the octyl chain of the imidazole/pyridine-based complex, **21c**, with the 3,5-difluorobenzyl group to afford **21d**, produced an 8% increase in the J_{SC}. Furthermore, the removal of the alkoxyl group from the latter produced a further enhancement in the conversion efficiency (η = 7.24%).

Surprisingly, we have only found two reports in which the luminescent properties of osmium(II)-NHC complexes were studied. Wong and coworkers prepared Os(II)-NHC complexes bearing different N^N ligands such as bpy and phenanthroline (Fig. 10).[37] In their first study, complexes **22** exhibited high-energy absorption at λ ≤ 300 nm and moderately intense bands at λ ≥ 330 nm, which were ascribed as IL and MLCT transitions, respectively. All complexes were emissive upon excitation at 450 nm in acetonitrile at room temperature, with emission bands between 675-730 nm. Quantum yields and emission lifetimes were around 10^{-4}-10^{-2} and 10^1 μs, respectively, and they were dependent not only on the NHC or N^N ligand, but also on the polarity of the solvent used for the luminescence measurements.

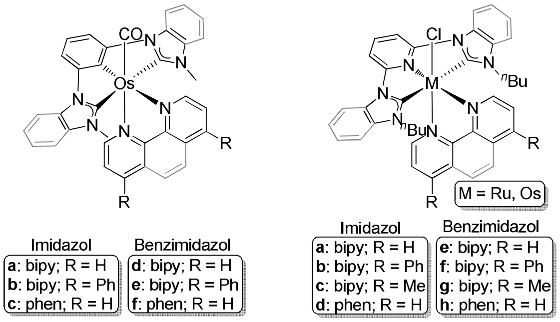


Fig. 10 Photoluminescent osmium(II)-NHC complexes.

In a related study, Wong studied analogous Ru(II) and Os(II) complexes bearing NHC/py-based ligands (**23**). All ruthenium(II) complexes were emissive with emission bands between 600-720 nm, and quantum yields and emission lifetimes of up to 10^{-3} and 10^3 ns, respectively, while none of the osmium(II)-NHC complexes prepared were luminescent.[38] Nevertheless, a great number of Ru(II)- and Os(II)-NHC complexes for OLED materials have been patented.[39-40]

Group 9: Rhodium and Iridium

In this group the chemistry of NHC luminescent complexes is dominated by Ir(III). Octahedral Ir(III) complexes coordinated to both cyclometallating (C^N) and NHC ligands or to NHC and other ancillary ligands are very stable compounds that exhibit relatively long-lived (microseconds time scale) and highly luminescent triplet excited states.

Only very few examples of emissive Rh(I) and Ir(I) species have been reported, and in each case the luminescence arises from the functionalisation of the imidazole ring. In this sense the presence of aromatic compounds with well-known photophysical properties provides the basis for luminescent transition metal compounds. A phenanthrene-fused imidazol-2-ylidene derivative and its Rh(I) and Ir(I) complexes **24** were described (Fig. 11).[41]

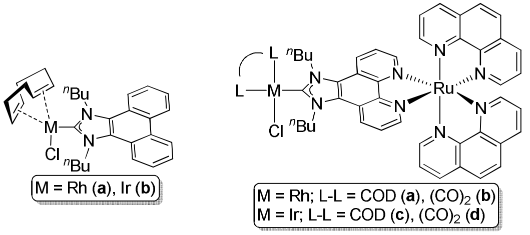
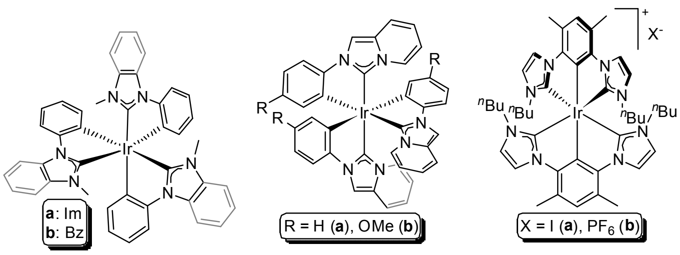


Fig. 11 Fluorescent Rh(I) and Ir(I) with phenanthrene or phenanthroline-fused NHC ligands.

The imidazolium salt showed a relative intensity three times stronger than that of the phenanthrene ligand, however, the complexes presented emission intensities very similar to that of the phenanthrene. The emissions of the imidazolium salt and the metal complexes were blue shifted compared to that of phenanthrene. Similar complexes with an imidazolyl ring fused to a phenenthroline produced heterobimetallic Ru(II)-M(I) (M = Rh, Ir) derivatives **25**.[42] These complexes exhibited ligand-based π–π and MLCT bands in the UV and visible regions, respectively. While mono-Ru was found to be emissive at 614 nm, blue-shifted emission bands ranging from 600 nm to 602 nm were observed for dinuclear complexes. Dinuclear complexes of the type Ru-M$(CO)_2$Cl had a stronger emission intensity and a higher luminescence quantum yield than those of Ru-M(COD)Cl. The complex Ru-Ir(COD)Cl could be employed as a CO detector because of the strong change in luminescence in the presence of CO. Emission intensity increased gradually suggesting that Ru-Ir(COD)Cl was slowly converted to Ru-Ir$(CO)_2$Cl by substitution of COD by CO.

A logical approach for the synthesis of complexes with blue and near-UV phosphorescence, reported by Thompson and coworkers, is the use of NHC ligands to form tris(cyclometallated) iridium complexes, starting from the basis that tris(cyclometallated) complexes with (C^N) ligands are excellent phosphors and substitution for a high field strength ligand such as the NHC could give rise to high energy emissions (Fig. 12). These complexes (**26** and **27**) were synthesised by direct reaction of $IrCl_3{\cdot}nH_2O$ in lower yield or through reaction with $[Ir(\mu\text{-}Cl(COD)]_2$ in high yield.[43-44] Complex **26,** as its analogue species $[Ir(C^\wedge N)_3]$ emitted from perturbed ^{3}LC states at high energies. These high emission energies, in conjunction with their low oxidation potentials, imply that these materials have high reduction potentials when in the excited state and consequently could be interesting candidates for use in photoinduced electron transfer studies.[43]



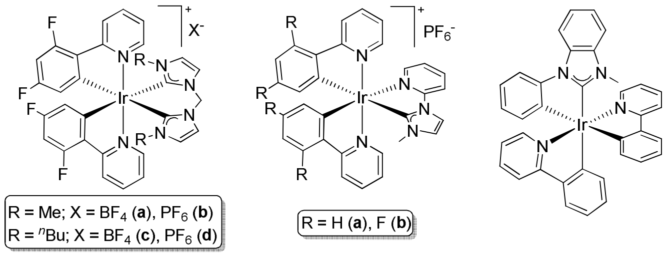
26 **27** **28**

Fig. 12 Blue and near-UV phosphorescent homoleptic Ir(III) complexes.

Efficient, saturated blue electrophosphorescence was achieved with the *fac-* and *mer-* **26** complexes doped into the wide gap host UGH2 (triphenyl-(4-triphenylsilylphenyl)silane). The colour obtained was a pure deep blue.[45]

Efficient near-UV emitters were also achieved by De Cola and coworkers with homoleptic bis(tridentate) Ir(III) complexes (**28**).[46] Tridentate pincer ligands of the type $C_{NHC}CC_{NHC}$ were used and the complexes were highly luminescent in acetonitrile solutions with quantum yields around 0.4.

A similar strategy to prepare iridium(III) blue phosphors exists in which NHCs are used as ancillary ligands to substitute one of the C^N species in the well-known tris(cyclometallated) iridium(III) complexes. Several derivatives were reported with substituted phenylpyridine ligands and different bis(carbene) or bidentate carbene species (Fig. 13).[47-49]



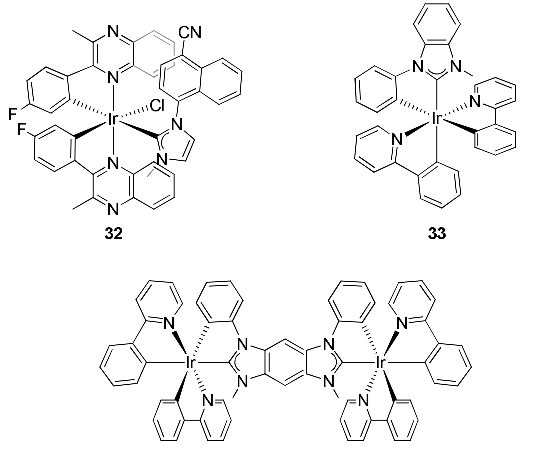
29 **30** **31**

Fig. 13 Several cyclometallated Ir(III) complexes with one bidentate NHC ligand

The emission properties of these charged C^N iridium(III) complexes (**29-31**) with carbene-based ancillary ligands were controlled mainly by the phenyl-pyridine C^N ligands, in contrast to the classical approach of charged complexes bearing chemically tuneable N^N ancillary ligands with low-energy π* orbitals. However, the results obtained with these complexes demonstrated the relevant impact of the ancillary ligand on the *Φ*, excited-state lifetime, and energy levels of this class of Ir(III) complexes. In contrast to the complexes based on the C^N ligands, no low-energy ^{3}MC state was localised, rationalising the larger values observed for the photoluminescence quantum yields.

A deep red triplet emitter derivative **32** was synthesised by Johannes and coworkers starting from the known cyclometallated complex with the ligand 2-(4-fluorophenyl)-3-methylquinoxaline. It presented a moderate quantum yield of 0.52 (Fig. 14).[50]

With the purpose of tuning the luminescent properties, bimetallic complexes with two cyclometallated phenylpyridine ligands and a ditopic NHC ligand, **34**, designed with the aim of some electronic communication were investigated by Bielawski and coworkers and compared with the monometallic complex **33**. The results showed that the coordination of the NHC ligand did not modify either the emissive state or facilitate interactions between the two units. The authors concluded that this could be a good approach to connect known phosphors through this type of ligand, which will function as a non-interfering ligand.[51]

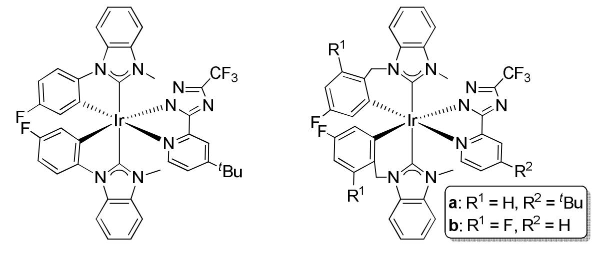


32 **33**

34

Fig. 14 Bis(cyclometallated) Ir(III) with an ancillary NHC ligand.

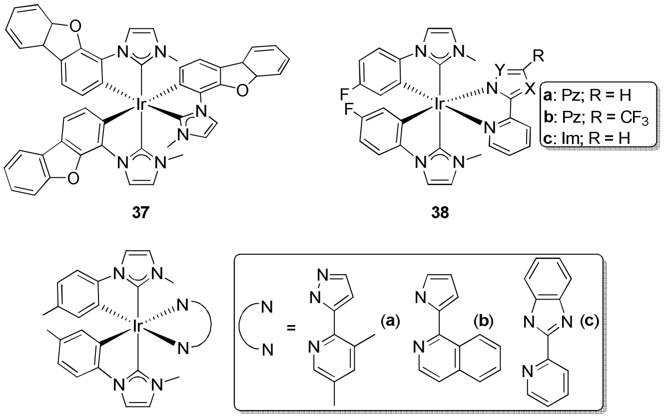
Heteroleptic Ir(III) complexes bearing two cyclometallated carbene and ancillary N^N ligands were reported by Wu and coworkers with different luminescent properties and potential applications. Complexes **35** and **36** were prepared by transmetallation of the benzyl carbene derivative over $[IrCl_3(tht)]$ (tht = tetrahydrothiophene) followed by addition of the bidentate pyridyl azolate ligand (Fig. 15). These complexes showed blue emission with maxima around 460 nm. The nature of the emissive state was analysed by TD-DFT calculations showing a mixture of a π-π* transition on the pyridyl azolate, an LLCT (fluorophenyl to the azolate fragment) and an MLCT (metal to pyridyl azolate) transition. One of them presented a high quantum yield of 0.73 and was used as dopant for fabrication of a blue phosphorescent OLED, showing unprecedented Commission Internationale de l'Elcairage (CIE) coordinates (0.16, 0.13).[52]



35 36

Fig. 15 Bis(carbene) Ir(III) compounds as highly phosphorescent blue OLEDs.

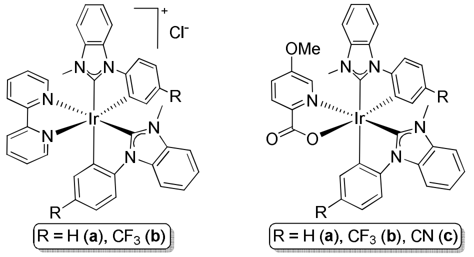
Modifications carried out on these complexes either in the pyridyl azolate ligand or in the substituents of the NHC ligand, allowed the synthesis of complexes **37**-**39** (Fig. 16) with a wide range of emission colours from blue to red with energies spanning from 455 to 599 nm, the N^N ligand being the main cause of this change. The devices prepared using these derivatives as dopants showed excellent external quantum efficiency from 17.1 to 24.9 %, which are among the highest values found.[53-55]



37 38 39

Fig. 16 Bis(carbene) Ir(III) compounds with azolate ligand as blue to red phosphorescent OLEDs.

The second family of complexes were prepared by Zhou and coworkers with substituted benzyl carbene ligands and bypiridine (**40**) and 5-methoxypicolate (**41**) as ancillary ligands (Fig. 17). The neutral and cationic complexes showed strong π-π* intraligand absorption bands in the range 250-300 nm and weaker MLCT transition bands from 350 to 450 nm. The emission energies spanned from 500 to 620 nm. This multicolour luminescence together with the low toxicity and good cell-permeability make them suitable for use as living cell imaging agents.[56]



40 41

Fig. 17 Luminescent Ir(III) complexes suitable as living cell imaging agents.

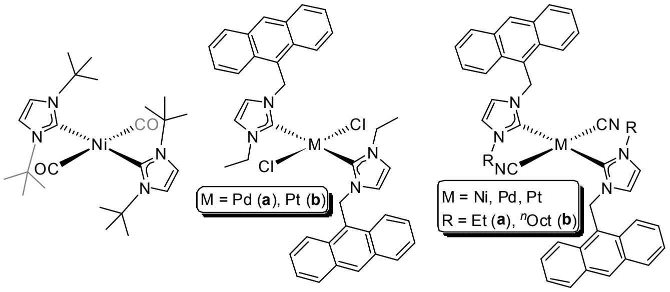
Group 10: Nickel, Palladium and Platinum

Luminescent group 10 metal complexes are mainly based on platinum species and only a few examples have been described for nickel or palladium.

The first luminescent example for nickel is a Ni(0) derivative reported by Vogler and coworkers in 2003.[57] The complex $[Ni(CO)_2(I^tBu)_2]$ (**42**), where I^tBu is a *tert*-buthyl substituted imidazolylidene, displayed an emission at 510 nm at room temperature, which was assumed to originate from the lowest energy MLCT triplet (Fig. 18).

Luminescent palladium(II)- and platinum(II)-carbene complexes were first reported by Zhang and coworkers in 2003.[58] The complexes contained an organic chromophore as a substituent on the carbene ligand, and the latter only acted as a linker between the chromophore and the metal (**43**). Although the luminescence for these compounds was based on the ligand itself, it was stronger for the metal complexes than for the free ligand.

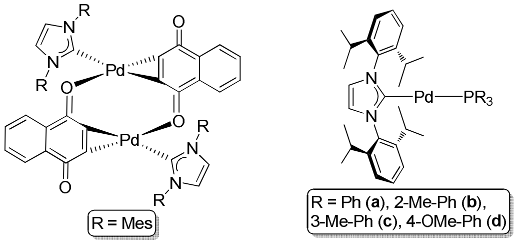
Similar complexes were described for Ni(II), Pd(II) and Pt(II) with CN^- ligands rather than chloride.[59] These complexes (**44**) were luminescent and their emissions were anthracene based but with stronger intensities than the corresponding imidazolium salts.



42 43 44

Fig. 18 First examples of luminescent group 10 complexes.

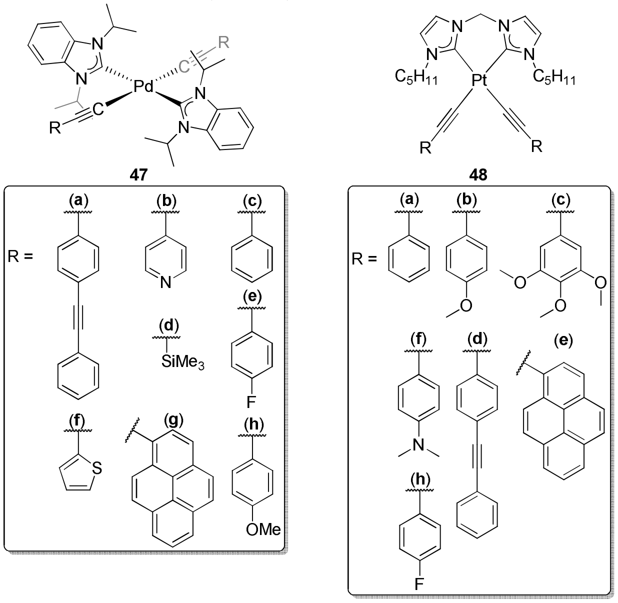
Pd(0) complexes were prepared with quinone and tertiary phosphine ligands (Fig. 19). The quinone derivative **45** presented two absorption bands at 312 and 399 nm assigned to LLCT (NHC→quinone) and MLCT (Pd^0→quinone). The complex was emissive at 77 K (λ_{max} = 564 nm) but not at r.t. where a photoredox decomposition initiated by the LLCT state took place.[60] The phosphine derivatives **46** were photoluminescent with energies of around 515-540 nm. The lifetime studied for complex **46b** showed a value of 160 ns, suggesting that the emissive excited state had a triplet character (Pd→phosphine) ^{3}MLCT.[61]



45 46

Fig. 19 Luminescent Pd(0) NHC complexes.

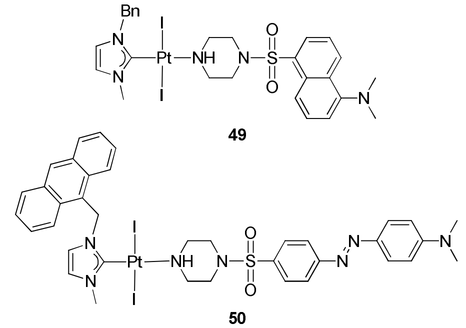
Pd(II) and Pt(II) complexes with *cis* or *trans* bis(acetylide) and bis(carbene) ligands were synthesised by Venkatesan and coworkers and their photoluminescence properties studied (Fig. 20).[62-63] The UV-Vis spectra for the palladium complexes **47** revealed great spectral changes depending on the nature of the acetylide ligands. The platinum complexes **48** were emissive at room temperature and the TD-DFT studies confirmed tunable lowest lying emissive states, assigned as predominantly metal-perturbed ligand-to-ligand ^{3}LLCT ($\pi_{alk}\rightarrow\pi_{alk}$) character and to a lesser extend ^{3}MLCT ($d\rightarrow\pi_{alk}$).



47 **48**

Fig. 20 Bis(acetylide)-bis(carbene) Pd(II) and Pt(II) complexes.

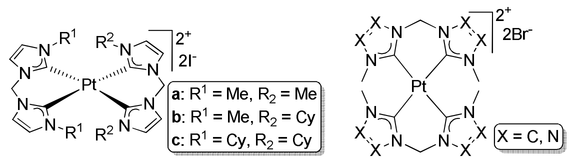
Substitution reactions on platinum NHC complexes bearing a labile pyridine ligand proved to be a versatile and highly selective method towards the coordination of amino groups as seen in compound **49** (Fig. 21).[64] These compounds could be of biological interest. Complex **50**, in which emission was switched on upon ligand exchange, could be an interesting tool to better understand the interaction between Pt-NHC complexes and DNA.



49 **50**

Fig. 21 Pt(II)-NHC complexes with amines with potential biological interest.

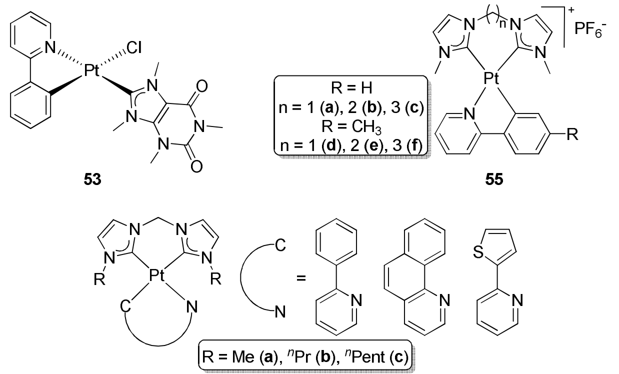
Platinum tetra(carbene) complexes were synthesised by Strassner and coworkers through different routes. In one route, the bis(carbene) diacetate intermediate complexes allowed the synthesis of mixed tetracarbene species **51** based on bis(imidazol-2-ylidene) ligands (Fig. 22). These complexes had moderate quantum yields and emitted in the near-UV region.[65-66] The change for bis(triazoline-5-ylidene) ligands to give **52** moved the emission wavelength to the visible region of the spectra.[67]



51 **52**

Fig. 22 Tetra(carbene) Pt(II) complexes.

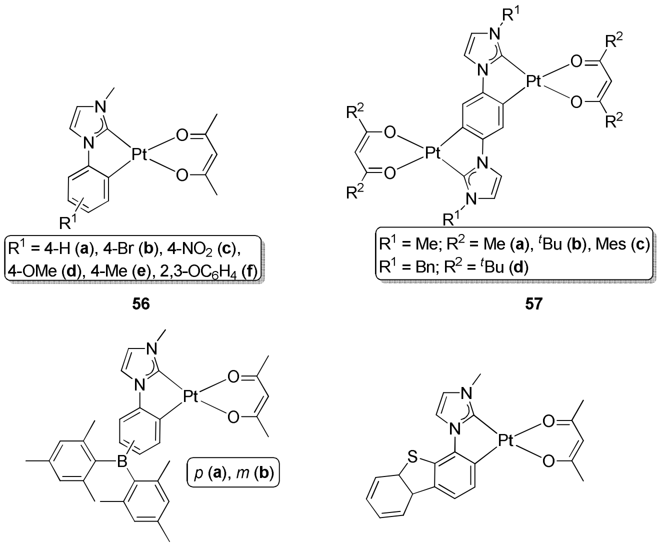
Other types of highly luminescent Pt(II) complexes are those based on cyclometallated complexes with NHC ligands. Several reports have dealt with their synthesis, including carbene ligands derived from caffeine **53,**[68] bis(carbene) derivatives with several N^C ligands **54**,[69] which have been found to selectively localise to the endoplasmic reticulum and induce stress and cell apoptosis, showing potent phototoxicity to cancer cells, or bis(carbene) and phenyl-pyridine derivatives **55**, which showed strong emission in fluid media (Fig. 23).[70]



53 **55** **54**

Fig 23 Several Pt(II) complexes with cyclometallated and NHC ligands.

Cyclometallated (C^C) platinum(II) *N*-heterocyclic carbene complexes with β-diketonate ligands of the form [(NHC)Pt(β-diketonate)] were reported and were also the subject of several patents (Fig. 24).[71-72] Complexes such as **56** showed blue emissions with the exception of the *p*-NO_2 substituted phenyl ring derivative which led to an emission maxima at about 550 nm. Complexes with strongly donating groups in the phenyl ring showed good quantum yields and were used in the construction of devices which displayed good CIE coordinates for blue components in white OLEDs.[73] The bimetallic complexes **57** emitted in the blue-green region of the visible spectrum and showed quantum yields of up to 93% together with shorter decay lifetimes compared to the corresponding mononuclear complexes. DFT studies revealed an MLCT/IL transition centred on the NHC ligand. The performance in a light-emitting diode was tested for some of these derivatives with **57a** giving the best results, showing an external quantum efficiency of 8.5%.[74]

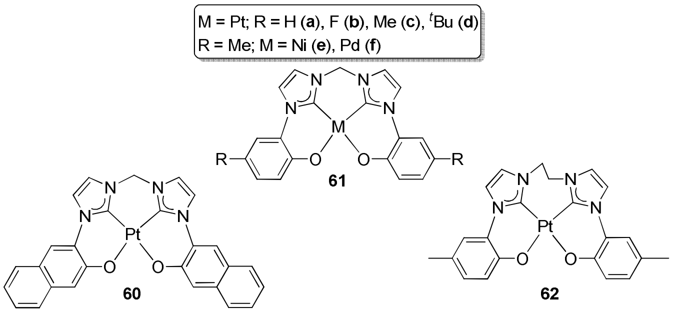


56 **57** **58** **59**

Fig. 24 Pt(II)-NHC complexes with β-diketonate ligands.

Boron funtionalised NHC chelate ligands and their acetylacetonate Pt(II) complexes **58** were reported and displayed highly efficient blue-green phosphorescence with quantum yields in the solid state of 0.86 and 0.9. Electroluminescent devices were constructed with these compounds, showing high external efficiencies of 17.9% for the *para* substituted and 9.8% for the *meta* substituted derivative.[75] The presence of a conjugated dibenzothiophene substituent in the cyclometallated complex **59** was proposed as the reason for the obtention of a high quantum yield of 0.63. This complex was also found to be a blue-green emitter and DFT calculations showed that emission was mainly based on the NHC ligand with a significant metal contribution (MLCT/LLCT).[76]

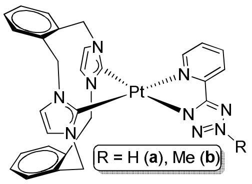
A series of Ni(II), Pd(II) and Pt(II) complexes **60-62** bearing bis(anionic) tetradentate bis(NHC) were prepared by Che and coworkers (Fig. 25). Crystallographic and DFT calculations revealed that the metal as well as the σ-donor strength, structural rigidity and geometry distortion of the tetradentate ligand were essential in tuning the frontier molecular orbitals and hence the luminescence properties.[77-78] The complexes were deep blue emitters and highly efficient blue- and white-light emitting OLEDs were prepared with the platinum ^{t}Bu derivative **61d**.



61 **60** **62**

Fig. 25 Deep blue M(II) emitters with tetradentate bis(NHC) ligands.

A square planar derivative with an *ortho*-xylene-linked bis(NHC)cyclophane and a 2-pyridyltetrazolate ligand **63** displayed a deep blue phosphorescent emission originating from excited states of ^{3}LC origin, involving the 2-pyridyltetrazolate ligand and partially mixed with ^{3}MLCT states (Fig. 26). The strong σ-donating properties of the carbene ligand and the coordination to the nitrogen atom of the tetrazole ligand destabilised the ^{3}MC level, thus enhancing the quantum yield of the complex in relation to other blue Pt emitters. Methylation of the complex took place in the tetrazole ring and changed the nature of the emitting excited state, which became predominantly ^{3}MLCT with significant reduction of the quantum yield.[79]

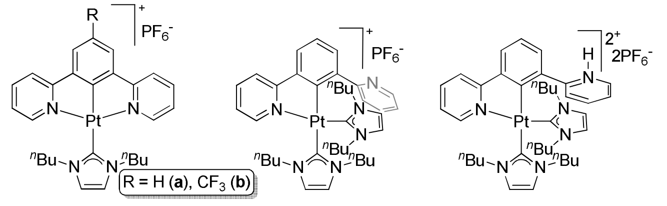


63

Fig. 26 Bis(NHC) Pt(II) complexes with a pyridyl-tetrazole ligand.

Cyclometallated pincer-type platinum complexes are known for their extraordinary photoluminescence because of the σ-donating property of the anionic carbons which effectively raises the energy of the d-d states, diminishing their deactivating effect. There are two types of these cyclometallated Pt derivatives with NHC ligands. The first are those bearing a cyclometallated C^N^C ligand and an ancillary NHC ligand, and the second those with the NHC forming part of the pincer ligand.

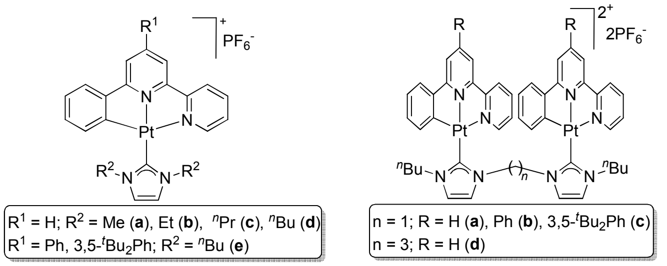
The reaction of the platinum pincer compound [PtCl(N^C^N)] with 1,3-bis(n-butyl)imidazolium bromide in different molar ratios and in the presence of a base gave complexes **64** or **65** (Fig. 27). In **65** the pincer ligand is in an η^2-coordination mode with a free pyridine unit, which after protonation afforded complex **66**. Complexes **64** were luminescent in solution and solid state, whereas **65** and **66** were weakly emissive in solution but in the solid state both presented the same emission, although that of **66** had much higher intensity and a much longer lifetime. This property makes this compound suitable as a solid-state sensor of acidic vapours.[80]



64 **65** **66**

Fig. 27 Cyclometallated pincer-type Pt(II) complexes with NHC ligands.

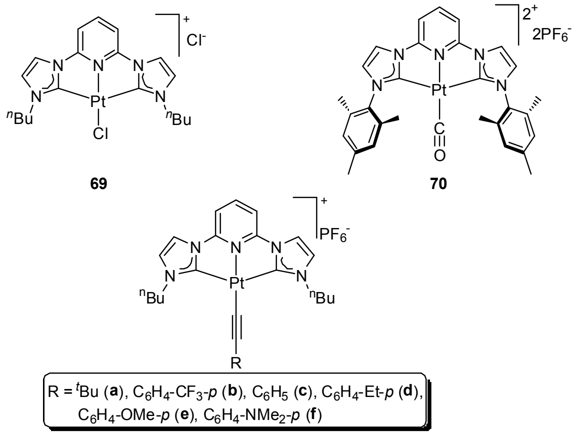
Other cyclometallated C^N^N platinum complexes were reported to be strongly emissive and stable under physiological conditions (Fig. 28). Complex **67d** was a potent anticancer agent with cytotoxic activity higher than that of cisplatin. It accumulated preferentially in cytoplasmic structures and could act as a surviving suppressant in triggering activation of poly(ADP-ribose) polymerase and hence apoptosis in cancer cells.[81]



67 **68**

Fig. 28 Cyclometallated C^N^N Pt(II) complexes with NHC ligands.

A Pt(II) complex with a pyridine-based pincer-type *N*-heterocyclic carbene ligand [PtCl(C^N^C)] **69** was a highly emissive luminophore and showed an aquachromic behaviour (Fig. 29). In the solid state the complex with 2.5 hydrate displayed an intense orange emission at 614 nm, whereas the anhydrous compound displayed bright green emission at 550 nm. These two colours could be reversibly switched through hydration and dehydration.[82] A similar complex **70** also showed a vapochromatic behaviour. Its emission was very sensitive to the presence of small donor molecules such as acetone, diethyl ether, THF, water or methanol, which caused a change of emission from blue to yellow.[83] Yam and coworkers reported the cyclometallated bis(carbene) Pt(II) complexes **71** bearing an alkynyl ligand. These complexes exhibited strong ^{3}MLCT/^{3}LLCT phosphorescence in degassed acetonitrile with the emission energy tuned by the different alkynyl ligands. Furthermore, the incorporation of these alkynyl groups was thought to play an important role in the enhancement of the luminescence.[84]

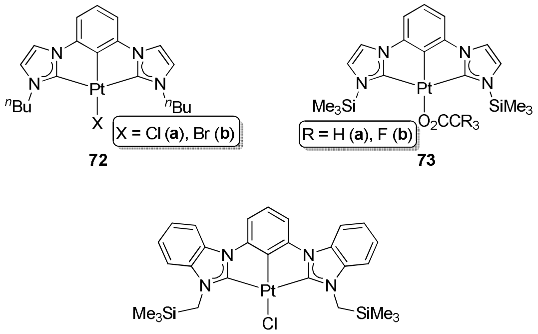


69 **70**

71

Fig. 29 Cyclometallated C^N^C based NHC Pt(II) complexes.

Hollis and coworkers prepared several cyclometallated C^C^C based NHC Pt(II) complexes and their emissive properties have been studied. The compounds were synthesised from direct metallation using $Zn(NMe_2)_4$ and transmetallation to platinum with $[PtCl_2(COD)]$ (Fig. 30).[85-88] Complexes **72** emitted bright blue light under and ambient atmosphere (O_2 and H_2O) for extended periods. They were also found to be thermally stable under N_2 atmosphere upon evaporation, which means that they would be suitable for thermodeposition processing.[85] Reaction of similar complexes with silver salts produced the simple ligand metathesis reaction as **73** or the formation of Pt_2Ag_2 clusters, which showed concentration dependant luminescence.[87] DFT studies were performed on **74** showing that the blue emission originated from a transition from a triplet excited state to the ground state. The time-dependant solid-state emission spectrum indicated that even though the emission is degraded by 14 % over 6 h in air, it was the most resistant to photobleaching compared with other emitters.[88]



72 **73**

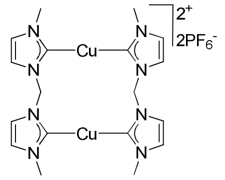
74

Fig. 30 Cyclometallated C^C^C based NHC Pt(II) complexes.

Group 11: Copper, Silver and Gold

Among all transition metal-NHC complexes with optical properties, those of group 11 have been the most extensively studied, especially complexes of gold(I). Since the first report of a luminescent Au(I)-NHC complex by Lin and coworkers,[89] many scientific groups have focussed their efforts on synthesising and studying group 11 NHC complexes with optical properties. In 2009, a review containing an interesting overview of the catalytic, medicinal and luminescent properties of coinage metal complexes to that date was published.[4]

In this review, we will only cover group 11 NHC complexes published since 2009, in which curiously the first example of a luminescent copper complex containing a NHC ligand is found, reported by Tsubomura and coworkers (Fig. 31).[90]

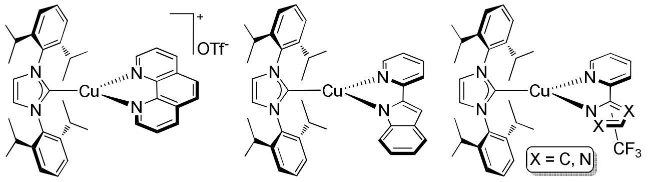


75

Fig. 31 First example of a luminescent Cu(I)-bis(NHC) complex.

The absorption spectrum of complex **75** showed a strong absorption band at 260 nm and another weaker shoulder at around 300 nm. Upon excitation at 320 nm, **75** displayed a blue-green emission centred at 482 nm in the solid state at room temperature with a quantum yield of 0.43. The decay curve of the emission at 482 nm was fitted with a double exponential curve with emission lifetimes of 27 and 133 μs, which suggested a phosphorescent character of the luminescence of the dinuclear complex **75**.

One year later, Thompson and coworkers reported the first phosphorescent three-coordinate Cu(I) complexes bearing an NHC ligand, **76** and **77** (Fig. 32).[91] The electronic absorption spectrum of cationic complex **76** showed intense bands in the region 250-300 nm and a weaker band at 332 nm which were ascribed as LC and MLCT transitions, respectively, while a single intense absorption band at 335 nm was observed for the neutral derivative **77**, assigned to LC transitions. Both complexes were strongly emissive in the solid state, whereas in solution, luminescence properties were solvent-dependent. Thus, a powder sample of **76** showed a featureless band centred at 555 nm with Φ = 58% (τ = 33.1 µs), while a decrease of the luminescence in cyclohexane (τ = 13.4 µs, Φ = 1.4%) was observed.

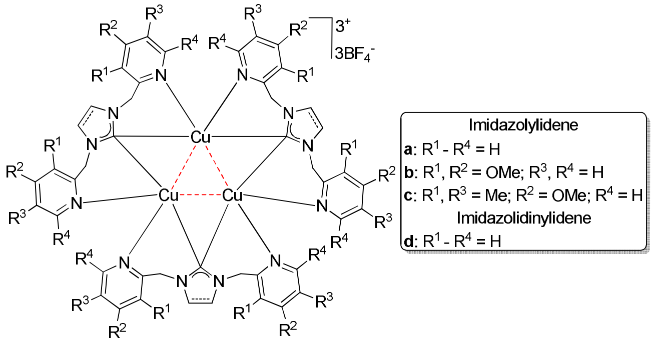


76 **77** **78**

Fig. 32 Phosphorescent three-coordinate Cu(I)-NHC complexes.

In a further study, analogous neutral Cu(I) complexes containing different pyridyl-azolate ligands were described (**78**).[92] The optical properties were very similar to those found for complex **76**. All complexes were emissive in solution at room temperature, displaying emission bands in the range 560-594 nm with excited-state lifetimes between 0.54-10 µs (Φ = 1.4-10%). Again, a significant enhancement of the emission occurred in the solid state, except for the complex without a CF_3 group, which showed a lower quantum yield value. The emission bands were found at around 565 nm with excited-state lifetimes between 12-13 µs (Φ = 23-62%), indicating the phosphorescent character of the luminescence.

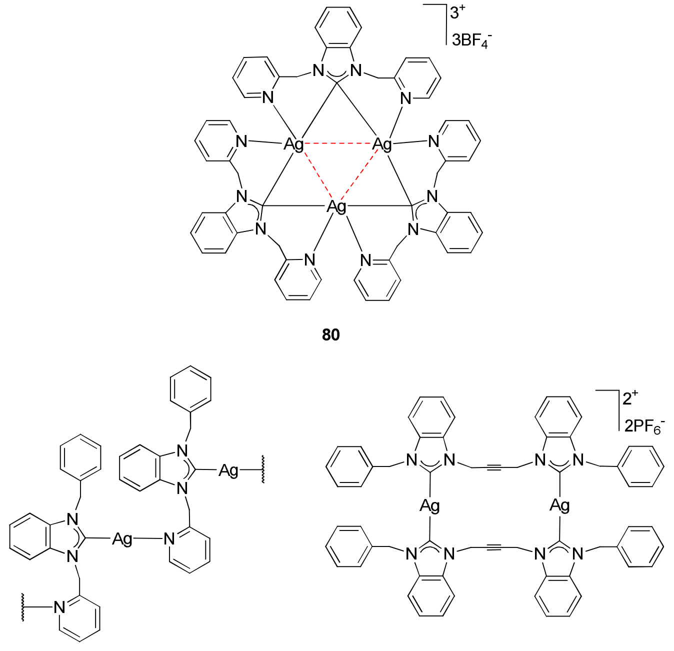
Catalano and coworkers studied the behaviour of the luminescence in different NHC-bridged triangular copper(I) complexes, **79** (Fig. 33).[93] They looked at the modulation of the metallophilic interactions between Cu atoms using different NHC ligands. All complexes exhibited an intense blue photoluminescence in solution, showing emission maxima from 427-459 nm. The complexes were also emissive in the solid state but no significant changes were observed compared to luminescence in solution. Although the assignment of the phosphorescent state was unclear, the blue emissions shown by these complexes make them good candidates for future applications as OLEDs.



79

Fig. 33 Emissive NHC-bridged triangular Cu(I) complexes.

Using different N-substituted benzymidazole ligands, Chen and coworkers prepared not only an analogous NHC-bridged triangular Ag(I) complex (**80**) but also the polynuclear complexes **81** and **82** (Fig. 34).[94] All complexes were emissive in acetonitrile at room temperature upon excitation with UV light. Unlike the trinuclear complex (**80**) which exhibited an intense band at around 460 nm, emissions of complexes **81** and **82** were blue-shifted, with maxima at 410 and 305 nm, respectively.

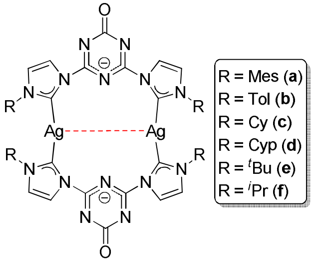


80

81 **82**

Fig. 34 Photoluminescent polynuclear silver(I)-NHC complexes.

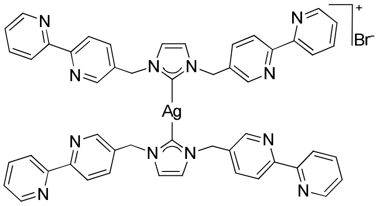
By varying the substitution pattern of the N-substituents of the imidazolium ring, Strassner and coworkers prepared different neutral silver(I)-NHC complexes, **83** (Fig. 35).[95] Although the electronic absorption of the complexes followed the same pattern, the emission properties were significantly influenced by the substituents. Thus, the emission bands for complexes **83** were found between 417 and 480 nm, and with excited-state lifetimes between 11.5-28.4 µs, which was in agreement with the phosphorescent nature of the emissions. The authors also found a correlation between the emission wavelength and the Ag···Ag distance.



83

Fig. 35 Neutral Ag(I)-NHC complexes with optical properties.

Since bipyridine ligands are known to have great chelating character, Wu and coworkers studied the coordination behaviour of a bis-bipyridyl-substituted imidazolium ligand.[96] The subsequent variation of the silver to ligand ratio allowed complexes **84-86** to be obtained (Fig. 36). All complexes were luminescent in both the solid state and in solution, except for complex **86** which showed poor stability in solution. The emissions were assumed to originate from a mixture of IL and MLCT transitions. Complexes **84**, **85a** and **85c** showed featureless emission bands at around 470 nm in solid state at room temperature, while complexes **85b** and **86** showed structured emission bands, but with maxima centred at 532 and 515 nm, respectively. In their study, the authors found the counteranion had a significant effect on the coordination mode of the complexes and consequently on the optical properties. The luminescent lifetimes measured in acetonitrile (0.75-30 ns) indicated that the emissions were of a fluorescent nature.



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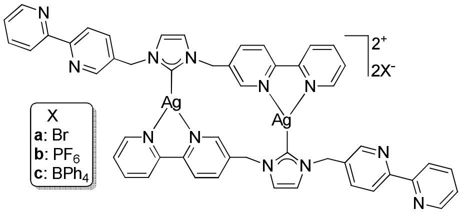

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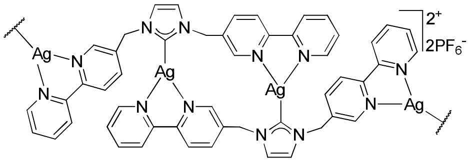
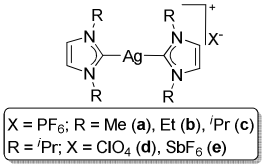


86

Fig. 36 Monomeric and polymeric silver(I) complexes containing a imidazole/bipyridine-based carbene ligand.

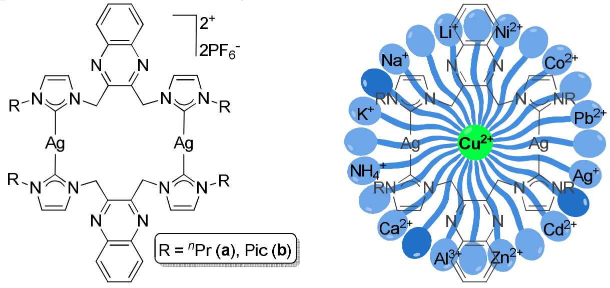
A large temperature dependence of Ag···Ag metallophilic interactions from a series of siver(I)-bis(NHC) complexes, **87**, was observed by Monkowius and coworkers (Fig. 37).[97] As expected, this temperature dependence had a notable effect on the optical properties of these complexes. Thus, except for **87b**, all complexes showed a blue-shifted emission upon cooling of solid samples from room temperature to 77 K. This phenomenon was more evident in complex **87d**, which featured a broad emission band at 484 nm at room temperature and at 358 nm at 77 K. A detailed analysis of the luminescence behaviour of **87d** revealed that upon warming from 77 K to room temperature, the recovery of the low-energy emission with a progressively decreasing intensity of the high-energy band was observed, showing an "isobestic" point at 420 nm.



87

Fig. 37 Silver(I)-bis(NHC) complexes with a temperature dependent luminescent behaviour.

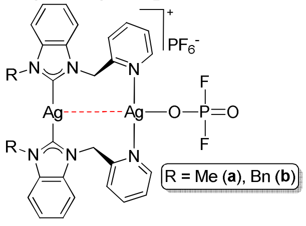
The design of new fluorescent chemosensors capable of selectively recognising guest species has become an important field within supramolecular chemistry.[98] The selective recognition of Cu^{2+} using complexes **88** as chemosensors was investigated by fluorescent titrations and UV-Vis titrations in acetonitrile at room temperature (Fig. 38).[99] Complexes **88** displayed a weak emission peak at 415 nm associated to the intramolecular excimer formation of quinoxaline. Surprisingly, upon addition of 5 equivalents of various different cations, no obvious change in fluorescence emission of **88** was observed, whereas after addition of an equivalent amount Cu^{2+}, a slight decrease of the emission band centred at 415 nm, and the appearance of a strong green-emission at 495 nm were detected. Thus, after titration of Cu^{2+} into solutions of **88**, the characteristic blue colour gradually decreased, giving rise to the appearance of an intense green-emission.

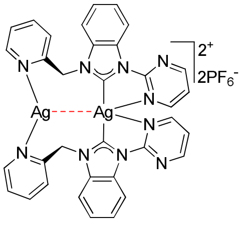


88

Fig. 38 Dinuclear silver(I)-NHC complexes as fluorescent chemosensors for Cu^{2+}.

Luminescent dinuclear silver(I)-NHC complexes, **89**[100] and **90**[101] derived from the 1-picolyl-benzimidazole were synthesised (Fig. 39). Although both complexes appear to have the same molecular structure in solid state, they showed different emission profiles in acetonitrile at room temperature. Complexes **89** exhibited emission bands at around 325-330 nm, while complex **90** displayed a strong emission peak at 450 nm. In both cases, the emissions were attributed to the existence of Ag(I)-Ag(I) argentophilic interactions.





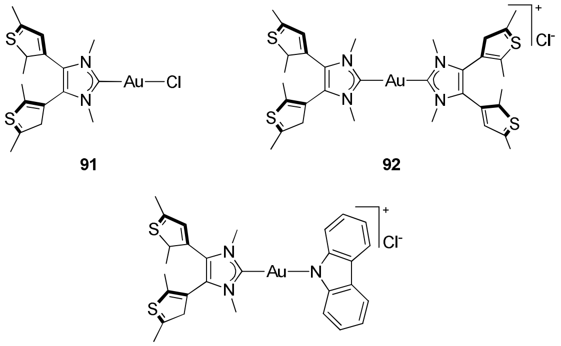
89 **90**

Fig. 39 Luminescent dinuclear Ag(I)-NHC complexes derived from the 1-picolyl-benzimidazole.

Luminescent gold-NHC complexes bearing electron-rich groups

As previously commented, since 2009 a great number of luminescent gold-NHC complexes have been reported, and their emissive nature is mainly due to the presence of electron-rich groups in the carbene ring, the presence of a chromophore ligand or an acetylide group directly bonded to the gold centre, the presence of metallophilic interactions, or appropriated energetic states characteristic of cyclometallated or three-coordinate species. In order to a better understand and discuss this topic, we have classified the photoluminescent gold-NHC complexes according to the origin of the emissions.

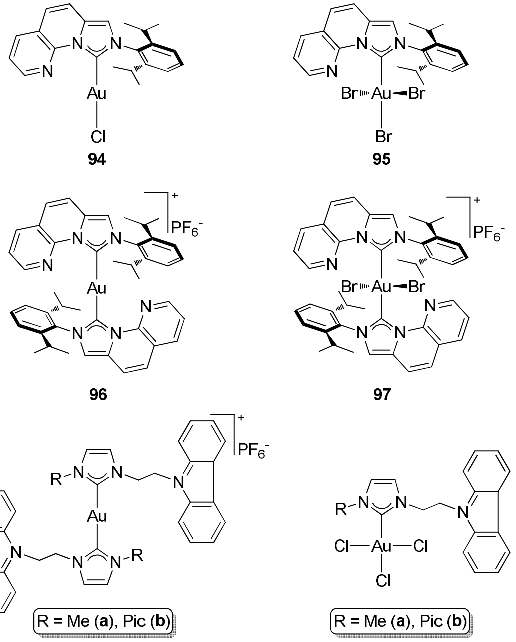
Similarly to complexes **9**, the presence of the arylethene groups in gold(I) complexes bearing NHC ligands conferred the optical properties characteristic of this type of compound. For example, the electronic absorption of complexes **91-93** showed intense maxima at around 230 nm in acetonitrile, which were ascribed to the metal-perturbed LC transitions of imidazole and thiophene rings (Fig. 40).[102] Additionally, complex **93** displayed a lower-energy absorption, which was assigned to the metal-perturbed LC transitions of the carbazole ligand. Upon excitation in the UV range of 200-300 nm, all complexes showed two new absorption bands at around 320-350 nm and 520-570 nm, which correspond to the closed form of the complexes **91-93** as a consequence of the photocyclisation of the diarylethene groups. The quantum yields for the photocyclisation reactions of the Au(I)-NHC complexes (0.21-0.47) were higher compared to that found for the imidazolium salt (0.19). In addition, a correlation between the electron donating ability of the ligand *trans* to the carbene ligand was observed, displaying an increase in the quantum yields in the order carbazolate (**93**) > NHC (**92**) > Cl (**91**).



91 **92** **93**

Fig. 40 Luminescent gold(I) complexes containing NHC-diarylethene ligands.

Monkowius and coworkers synthesised a phenanthroline analogue NHC ligand for the preparation of complexes **94-97** (Fig. 41).[103] As expected, the electronic absorptions of all complexes were similar to the precursor, and they were assigned to IL transitions. All complexes were luminescent in solution with both a structured high-energy and low-energy band. For example, complex **96** exhibited two emission bands in CH_2Cl_2 centred at around 400 and 550 nm, which were assigned as ^{1}IL and ^{3}IL transitions, respectively. In addition, Au(III)-NHC complexes underwent photoreductive elimination of Br_2 upon irradiation with polychromatic light affording the Au(I) congener.

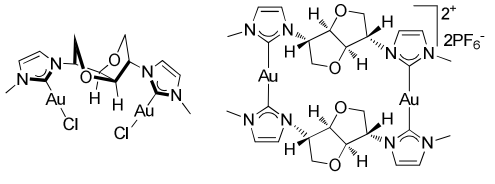


94 **95** **96** **97** **98** **99**

Fig. 41 Luminescent gold(I) and gold(III) complexes bearing functionalised NHC ligands with chromophore groups.

Carbazolate derivatives **98** and **99**, depicted in Fig. 41, showed similar emission profiles with emission bands between 380-450 nm.[104] All of them exhibited blue-shifted emissions compared to the precursor, which was attributed to the electron-withdrawing effect of gold that could inhibit the photo-induced electron transfer process of the lone-pair electron of the nitrogen atom to the carbazole ring.

Luminescence studies of dinuclear gold(I)-NHC complexes **100** and **101** revealed that both the neutral and cationic species were emissive in solid state with emission peaks at around 380 nm, and with emission lifetimes of 35 and 379 ns, respectively (Fig. 42).[105] By comparing their electronic absorptions (270-300 nm) with the precursor imidazolium salt, the emissions could be assigned as derived from metal-perturbed LC transitions. Furthermore, although complex **101** presented weak aurophilic interactions (Au-Au distance of 3.3248 Å), the photoluminescence results suggested that the presence or absence of such interactions did not affect the luminescent properties of the complex.



100 **101**

Fig. 42 Isomannide-bridged dinuclear gold(I)-NHC complexes.

Luminescence studies were performed for coinage metal complexes bearing acridine/NHC-based ligands (Fig. 43).[106] For all complexes (**102-104**), both the electronic absorption and the diffuse reflectance spectra showed similar bands to those found for the precursor imidazolium salt, which were attributed to the acridine π→π* or n→π* transitions. Solid samples of complexes **102-104** were blue-green emitters at room temperature and at 77 K showing emission bands between 470-530 nm, and most of them displayed another weaker shoulder at 390 nm. For complexes **101**, no significant changes were found on going from silver to gold, with only a slight red-shift (23 nm) observed. On the other hand, the copper derivatives **102a** and **102b** only showed the emission band at 390 nm, which was attributed to the destabilisation of the π* orbital of the acridine moiety. Pentafluorophenyl derivatives **103** displayed a different luminescent behaviour, since **103a** showed a blue-shifted emission (30 nm) centred at 500 nm, while complex **103b** showed a red-shifted emission (45 nm) centred at 515 nm related to the analogous chloride derivatives (**102**). In the case of bis-carbene species, silver(I)- and gold(I)-NHC complexes (**104**) exhibited shifted emissions upon replacing the methyl group for the benzyl group. The emission lifetimes for complex **103a** and its precursor salt were found to be around 35 ns, supporting a fluorescent character of the emissions. In addition, all complexes were found to be blue-emissive in solution upon excitation at 250 or 375 nm, displaying a structured band with maxima at 410 and 435 nm, and a weaker shoulder at 460 nm. These differences compared to the solid state could be a result of the absence of π-π staking interactions in solution.

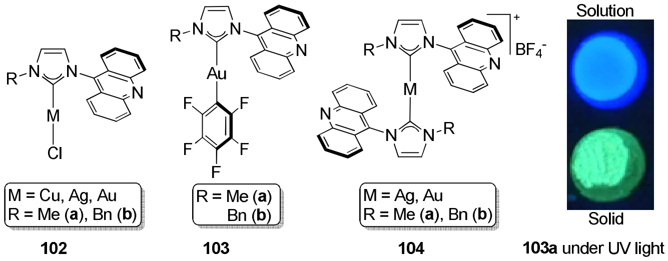


Fig. 43 Coinage metal complexes containing acridine/NHC-based ligands.

Luminescent gold-NHC complexes containing acetylide and chromophore groups bonded to the gold centre

In general, alkynylgold(I) complexes represent an interesting family of luminescent materials. Since gold(I) alkynyls are predominantly two-coordinate, the origin of the emissions they normally show is mainly derived from the triplet excited-state of the alkynyl ligand or from aurophilic interactions.[107] The facile incorporation of acetylide groups to the metal centre is also applicable for other organic functions. Thus, some research groups have focussed their efforts on preparing gold(I)-NHC complexes containing acetylide or aromatic groups such as pyridines or aromatic systems *trans* to the carbene ligand. Complexes **105** and **106** were easily prepared by in situ deprotonation of the corresponding terminal alkynes using the appropriate base (Fig. 44).[108] As expected, the electronic absorption spectra of complexes **105** exhibited intense absorptions between 248-258 and 350-390 nm (anthracenyl), and other absorption peaks between 280-320 nm (acetylide). These bands were assigned to π→π* transitions involving the anthracenyl ring and acetylide group, respectively. On the other hand, due to the absence of the anthracenyl group in complexes **106,** only absorption peaks at 230-380 nm were observed and were assigned to acetylide-based π→π* transitions.

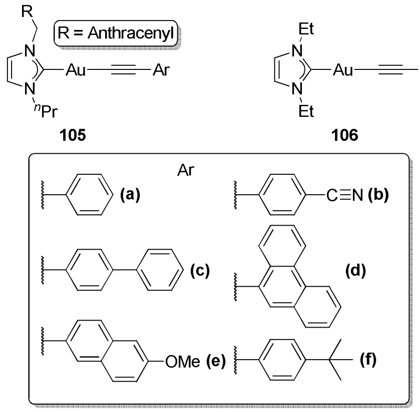


Fig. 44 Imidazolyl gold(I) alkynyl complexes bearing different chromophore groups.

All complexes (**105** and **106**) were emissive in degassed CH_2Cl_2 solutions and in the solid state, with the exception of complexes **106b** and **106e** which were not emissive in the solid state at room temperature. The anthracenyl derivatives (**105**) showed emissions between 394-443 nm in solution, similar to those found for the precursor imidazolium salt. Therefore, the authors assigned the emitting excited states of complexes **105** to be $^1\pi\rightarrow\pi^*$ excited states localised at the NHC ligand.[108] On the other hand, the emissions (lifetimes in μs) of complexes **106**, which lacked the anthracenyl group, were ascribed as $^3\pi\rightarrow\pi^*$ excited states localised at the arylacetylide ligand.

The electronic absorption spectra of complexes **107** displayed an absorption peak between 288-381 nm (Fig. 45).[109] All complexes except **107i** showed a structured emission in CH_2Cl_2 solutions with an intense band (371-525 nm) followed by another less intense shoulder in the lower-energy region. Complexes **107h** and **107k,** containing nonaryl groups, showed a very weak emission around 417 nm, which suggested that aryl groups could play an important role in the luminescent properties of this kind of complex. Although complexes **107c**, **107e** and **107j** showed aurophilic interactions in solid state, none of them showed any additional low-energy bands characteristic of MMLCT transitions. Excited-state lifetimes were found between 0.21-3.75 μs with quantum yields around 0.19-9.9%.

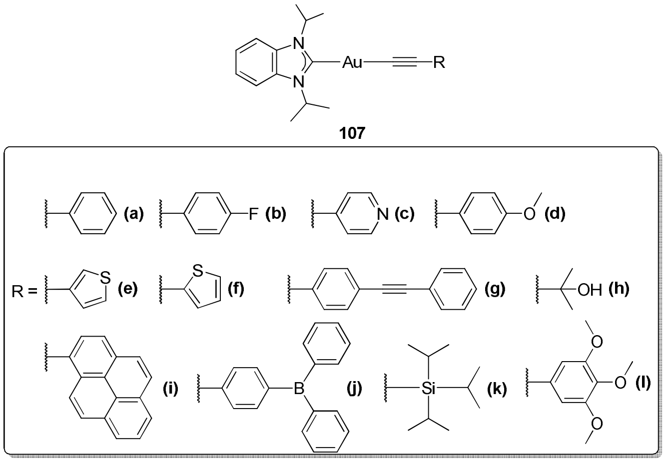
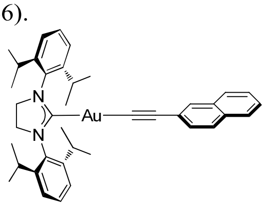


Fig. 45 Benzimidazolyl gold(I) alkynyl complexes.

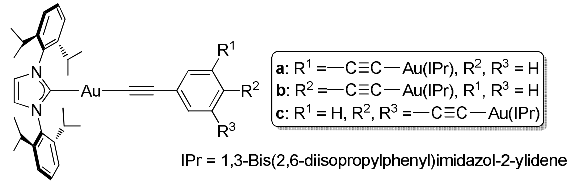
In a related study, Gray and coworkers synthesised and examined the photoluminescent properties of gold(I)-akynyl complexes bearing different phosphine and NHC ligands. Complex **108** showed the same emission profile as its analogues with PPh_3 and PCy_3, featuring absorption peaks at 315-330 nm and two structured emission bands centred at 362 nm (high-energy) and at 542 nm (low-energy).[110] The high-energy emission was assigned as an ethynylphenanthryl-centred singlet state (Fig. 46).



108

Fig. 46 Imidazolidinyl gold(I) alkynyl complex containing a naphthyl group.

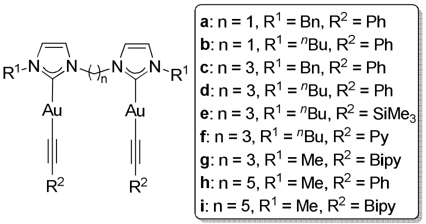
Unlike the complexes mentioned above, complexes **109** were synthesised using a versatile gold synthon for acetylene C-H bond activation (Fig. 47).[111] The electronic absorption spectra of complexes **109** showed similar absorption peaks centred at around 285 nm. Overall, complex **109a** exhibited more intense absorption and emission spectra, and appeared red-shifted (496 nm) compared to the spectra of complexes **109b** (439 nm) and **109c** (448 nm). Since aurophilic interactions in solid state were not observed, this red shift observed for **109a** was attributed to the elongated conjugation promoted by *para* substitution about the central benzene ring. In addition, the quantum yield for complex **109a** (0.17) was higher than those found for complexes **109b-109c**.



109

Fig. 47 Di- and trinuclear gold(I) alkynyl complexes.

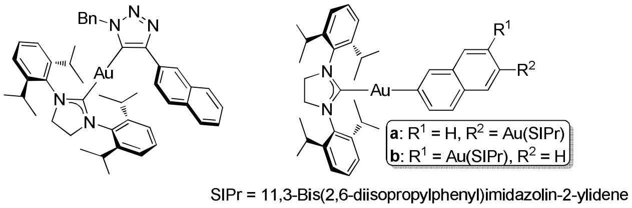
Gil-Rubio and coworkers prepared the first dinuclear gold(I)-alkynyl complexes containing bridging dicarbene ligands **110** (Fig. 48).[112] All complexes displayed two absorption bands, one in the high-energy region (around 240 nm) and another one in the range 257-332 nm depending on the substituent of the alkynyl unit, which were tentatively assigned to metal-perturbed IL transitions. All complexes except **110e** were luminescent in solution (305-536 nm) and in the solid state (370-585 nm) at room temperature, with emission lifetimes between 0.37-249.5 μs. In this case, the aurophilic interactions were reflected in the optical properties of the complexes, and some of them exhibited emission bands in the low-energy region, which were assigned to gold-perturbed ^{3}IL transitions.



110

Fig. 48 Dinuclear gold(I) alkynyl complexes bearing dicarbene ligands.

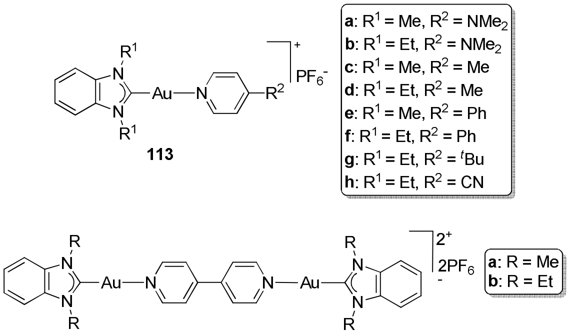
Complex **111** was prepared by means of a copper-catalysed [3+2] cycloaddition of complex **108** with benzyl azide (Fig. 44).[113] The electronic absorption spectrum showed two absorption peaks centred at 260 and 312 nm. Upon excitation at 312 nm, complex **111** exhibited two emission bands, one at 383 nm (high-energy) and another low-energy structured emission band with peaks at 498, 536 and 579 nm in THF solution. The lifetime measurement of 19.1 ms at 77 K for the latter indicated that this emission came from a triplet-state significantly influenced by the gold atom. Theoretical calculations found the frontier orbitals to lie mostly on the conjugated Tz ligand, suggesting that the optically allowed transitions were mainly intraligand and ligand-to-metal transitions. Another synthetic route to incorporate aromatic systems to [gold(I)-NHC]$^+$ species is the use of aryl boronate esters. For example, complexes **112** were prepared from the reaction of a [AuX(NHC)] precursor and the appropriate pinacolboronate ester in the presence of Cs_2CO_3.[114] Both complexes (**112**) were emissive in solution, displaying structured emission bands between 490-605 nm and with excited-state lifetimes ranging between 0.26-1.28 ms.



111 **112**

Fig. 49 Gold(I)-NHC complexes containing a naphthyl group.

Lin and coworkers studied the effect of different 4-substituted pyridines on several gold(I)-NHC complexes (Fig. 50).[115] The electronic absorption spectra of all complexes (**113** and **114**) in acetonitrile exhibited two major absorption bands at around 230 and 290 nm, and a weaker band at 250 nm. All complexes were emissive in solid state in the range 389-470 nm. Complexes **113a** and **113b**, which presented weak Au···Au interactions, displayed structureless emission bands at ca. 400 nm and a structured weak tail down to 600 nm. In addition, no trend in the red-shifting of absorption and emission bands related to the electron-accepting properties of the pyridine ligands was observed. Theoretical calculations on solid structure of complex **113a** suggested that the HOMO was associated with the pyridine ligands while the LUMO was predominantly of Au···Au interaction character.



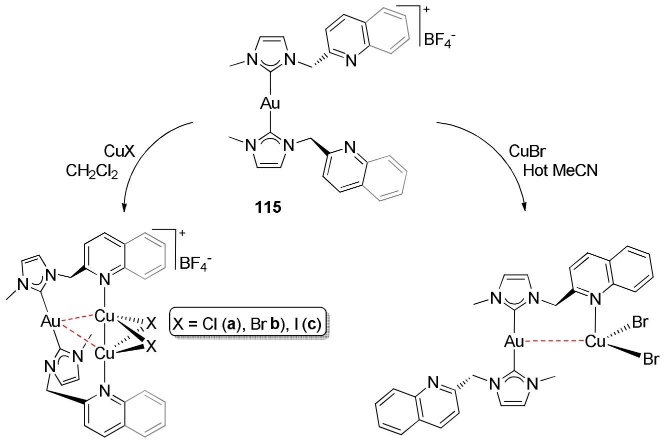
113

114

Fig. 50 Gold(I)-NHC complexes containing pyridyl and bipyridyl groups.

Luminescent properties of gold-NHC complexes promoted by metallophilic interactions

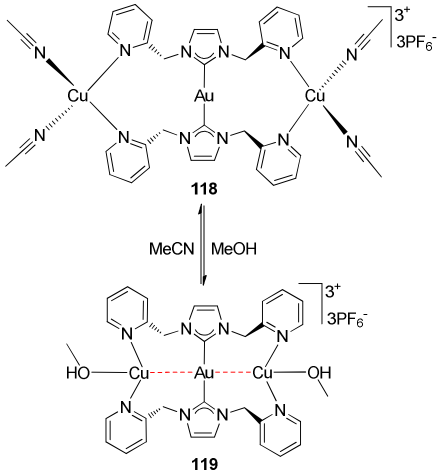
The presence of metallophilic interactions between d^{10} closed shell metal ions has attracted great interest not only for the design of clusters,[116] but also because of the luminescent properties they could confer to the final complexes.[117] Many research groups, taking advantage of the versatility of NHC ligands, have focussed on the design of photoluminescent gold-NHC complexes with particular metal interactions. For example, complexes **115** reacted with copper(I) halides in dichloromethane to form luminescent gold(I)-NHC complexes containing Cu(I)-X dimers, **116a-116c** (Scheme 1).[118] In all cases, the Cu_2X_2 cluster was held very close to the gold centre, showing different Au-Cu bond distances depending on the halide and the *N*-substituted ligand used. On the other hand, complex **117**, containing only one $CuBr_2$ molecule, also presented a metallophilic interaction with an Au-Cu distance of 2.9581(6) Å.



Scheme 1 Synthesis of gold(I)-NHC complexes containing copper(I) halide butterfly dimers.

All of the complexes in acetonitrile exhibited the same absorption maxima found for the corresponding precursor imidazolium salts. Complex **115** was highly emissive with one band at 612 nm, while complexes **117** derived from the quinoline showed emission bands between 535-583 nm upon excitation at 382 nm. The dimetallic species (**117**) displayed a notable red-shifted emission, exhibiting a unique emission band at 642 nm. Likewise, picolyl substituted complexes (**116**) showed the same emission profile to those found for the analogues with quinolyl, and emission maxima were found between 545-556 nm. The similar results found by changing from quinolyl- to picolyl-complexes, and the difficulty to measure the luminescent properties of the complexes in solution because of the dissociation of CuX, made assignment of the emissions inappropriate.

The vapochromic complex **118** was easily prepared by reaction of the corresponding gold(I)-bis(NHC) complex with two equivalents of $[Cu(MeCN)_4]PF_6$ in acetonitrile (Scheme 2).[119] Interestingly, this complex, which displayed an intense blue-emission at 462 nm in solid state, could react with MeOH vapour to afford the green-emissive species **119**, which emitted at 520 nm. This process was completely reversible and consisted in the modulation of the Au···Cu separation depending on the solvent molecule coordinated to the copper centre. Thus, the Au···Cu separation in complex **118** was ~4.6 Å, while for complex **119** it was significantly shorter (2.7915 (7) Å). This metal reorganisation was rationalised as a result of the absence of a second coordinating solvent molecule in complex **119**, in which each Cu centre completed its tetrahedral geometry by interaction with the gold centre. Also, upon exposure to air, a red-shifted emission at 543 nm was observed for compound **119**, while exposure to vacuum produced a spontaneously and notable luminescence change to yellow-orange with emission maximum at 573 nm. In addition, complexes **118** and **119** were sensitive to H_2O and Me_2CO vapours; while as expected, CH_2Cl_2 and THF vapours had no effect on the luminescent properties. The great properties of complexes **118** and **119** as vapochromic materials have led to a recent patent.[120]



Scheme 2 Vapochromic gold-NHC complexes.

Catalano and coworkers, in an attempt to reproduce the same results obtained for complexes **116**, tried to apply a similar procedure to synthesise butterfly Cu_2X_2 dimers with the symmetrical bis-carbene gold(I) complex derived from the imidazole/pycoline-based ligand, but this was unsuccessful.[121] They also found that the addition of two equivalents of CuX to bis-carbene derivative in acetonitrile produced the trimetallic species **120** (Fig. 51). Furthermore, the polymeric complex **121** was afforded after addition of four equivalents of CuBr to a warm solution of the bis-NHC precursor. Complexes **120** displayed green-emission bands between 502-512 nm, while for the polymeric derivative a red-shifted emission at 533 nm was observed. In this case, the emission maxima did not trend according to halide, however, the Au···Cu separations showed a good correlation with the observed emissions. Thus, complex **120b** with the shortest separation exhibited the highest energy emission, while the lowest energy emission corresponded to **120a**, which presented the longest Au···Cu separation. In addition, all complexes exhibited a notable increase of the emission intensity upon cooling to 77 K.

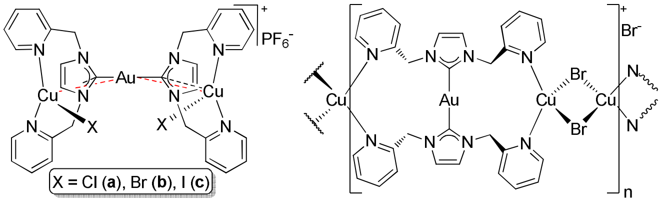
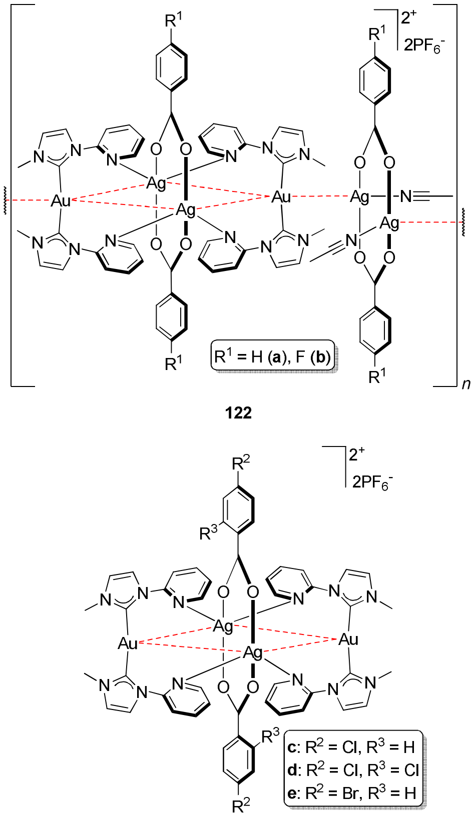


Fig. 51 Luminescent Cu(I) halide adducts of gold(I)-NHC complexes.

Au(I)-Ag(I) tetra- and polymetallic complexes **122** and **123** were synthesised by reaction of the corresponding unsymmetrical Au(I)-bis-(NHC) precursor with different substituted silver benzoate salts in acetonitrile (Fig. 52).[122] Both examples had discrete tetrametallic Ag_2Au_2 diamond cores. All complexes exhibited absorption bands into the UV region between 219 and 240 nm, however none of them were luminescent at room temperature. In frozen acetonitrile solution (77 K), complexes **122** were emissive, displaying emission bands at ca. 490 nm, while for the tetrametallic assemblies the emission bands were red-shifted (500-506 nm).

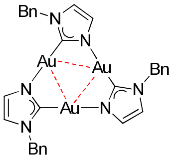


122

123

Fig. 52 Luminescent Au(I)-Ag(I) tetra- and polymetallic complexes.

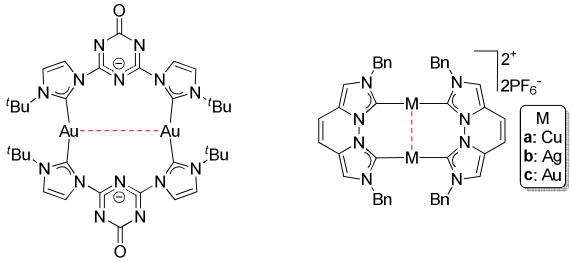
Rawashdeh-Omary and coworkers reported the structure of the well-known trinuclear gold(I) complex **124** (Fig. 53), which crystallised with two symmetric molecules associated as dimer-of-trimer units, stabilised by aurophilic interactions.[123] The interaction with the organic π-acid perfluoronaphthalene ($C_{10}F_8$) was investigated. Crystals of complex **124** were brightly luminescent in solid state at room temperature (λ_{em} = 500 nm), and a pronounced increase in the intensity and lifetime (from 7.8 to 23 μs) was observed. The origin of this emission was assigned to ^{3}MC transition derived from a largely distorted excimeric triplet state. Moreover, a great change in the emission profile of the **124**$\cdot C_{10}F_8$ adduct was observed, going from a green featureless phosphorescence to a yellow structured emission at 550 nm. Also, there was a pronounced enhancement of the emission lifetime reaching up to 1.8 ms, confirming the phosphorescent character of the emissions.



124

Fig. 53 Luminescent trinuclear Au(I)-NHC complex.

As for complexes **83**, the analogous neutral dinuclear gold(I)-NHC complex (**125**) was prepared by Strassner and coworkers from the corresponding silver precursor (Fig. 54).[124] The electronic absorption spectrum of complex **125** showed different absorption maxima at around 220, 270 and 310 nm, and compared with its silver analogue **83**, **125** exhibited a red-shifted emission at 464 nm in the solid state. They also found a slight blue shift when comparing with film (2%), which was attributed to a small increase of the intramolecular aurophilic interactions as a result of geometrical changes in the complex due to the packing effects.



125 **126**

Fig. 54 Luminescent neutral and cationic dinuclear coinage metal NHC complexes.

Cationic dinuclear coinage metal complexes **126** were prepared from a 1,10-phenanthroline analogue pyridazine-based NHC ligand.[125] The excitation spectra for all complexes in dichloromethane exhibited absorption bands between 354-381 nm, and a second one for complex **126c**. Upon excitation at the corresponding excitation band, all complexes were emissive. For example, complexes **126a** and **126b** displayed almost identical emission bands centred at ca. 445 nm, while the gold derivative (**126c**) showed a structured red-shifted emission band with peaks at 521 and 563 nm, and a shoulder at 610 nm, a characteristic effect for complexes containing aurophilic interactions.

A series of photoluminescent dinuclear bridged Au(I)-NHC complexes are shown in Fig. 55. In all these complexes, the large and flexibility of the NHC ligands facilitated contact between the gold centres, and consequently, the appearance of noteworthy luminescent properties. For example, complexes **127** were emissive in both solution and the solid state.[126] There was a substantial enhancement in the intensity of the emission going from solution to the solid state, especially for complex **127a**, which remarkably reached a quantum yield of 96%. The emission lifetimes for complexes **127a** and **127b** were found to be of 565 and 132 ns, respectively. Furthermore, **127a** showed emission bands at 374, 450 and 488 nm in acetonitrile, room temperature solid state and 77 K rigid matrix, respectively, which were associated to a tuning of the Au···Au distance under different conditions. In further work, Hemmert and coworkers studied the influence of anions on the Au···Au interactions in complexes **128** (Fig. 55).[127] X-ray diffraction analysis of complexes **128** revealed that the halide anions form hydrogen bonds with the N-H groups of the side arms and DFT calculations suggested that such an interaction could influence the Au···Au distances. However, such an influence was not reflected in the optical properties of the complexes. Thus, the electronic absorption and emission spectra for complexes **128** were very similar to those found for the precursor imidazolium salts, exhibiting absorption bands at around 245 nm, while blue-emissions were found at ca. 390 nm in a rigid matrix at 77 K in water and acetonitrile. The emission lifetimes found for the precursor (τ = 0.66 s) and **128a** (τ = 0.90 s) suggested a phosphorescent character of the emissions, and this difference was attributed to the presence of aurophilic interactions.

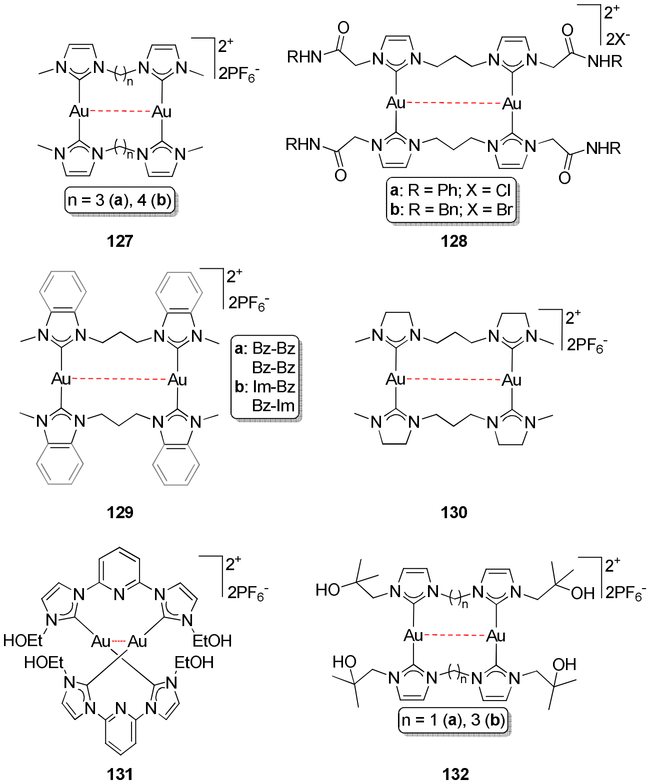
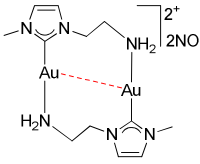


Fig. 55 Luminescent dinuclear bridged gold(I)-NHC complexes.

Tubaro and coworkers synthesised complexes **129** and **130** in order to compare and study their optical properties relative to **127a** (Fig. 55).[128] Complexes **129** and **130** exhibited absorption bands between 250 and 400 nm attributed to π→π* LC transitions, and with emission bands falling in the range 400-500 nm with τ = 0.25-2.5 μs. Unfortunately, none of these complexes were found to be as emissive as **127a,** even complex **129b**, which was characterised by the smallest Au···Au distance. A red-shift (50 nm) was observed when comparing the saturated derivative (**130**) with its unsaturated analogue (**127a**), which suggested that the emissive properties could be influenced by the electronic properties of the NHC ligand.

There are few reports of gold complexes with short metal-metal contacts which are luminescent in solution. Therefore, some groups have focussed their efforts on this goal. For example, Hemmert and coworkers synthesised dimeric dinuclear gold(I) complexes bearing different alcohol-functionalised NHC ligands (**131** and **132**).[129] All complexes displayed absorption bands between 216-282 nm in acetonitrile, characteristic of π→π* LC transitions, while the corresponding emission bands were found in the high-energy range of 328-446 nm, with another low-energy band (except **132b**) centred at 526 nm, which were assigned to IL and MC transitions, respectively. Moreover, the corresponding gold(III) species also showed luminescence in solution with emission maxima between 312-382 nm, however assignment of the emissions was not possible.

Finally, Cassani and coworkers used an amino-functionalised NHC ligand to prepare a luminescent dinuclear gold(I) complex (**133**) containing aurophilic interactions (Fig. 56).[130] Its emission spectrum exhibited a featureless band at 410 nm upon irradiation at both the absorption wavelength (236 nm) and the excitation band (260 nm) in solution. Surprisingly, upon excitation of **133** in solution at 297 and 330 nm, new bands at 367 nm with a different emission profile were observed. These results were attributed to the presence of aurophilic interactions, which were assumed to be maintained in solution.



133

Fig. 56 Photoluminescent amine-functionalised NHC gold(I) complex.

Luminescent cyclometallated gold(III)-NHC complexes

Unlike gold(I) complexes, reports of luminescent organogold(III) complexes are sparse. The luminescence quenching commonly observed for these species is mainly attributed to the high electrophilicity of the gold(III) ion, which can promote d-d states that are energetically close to emissive IL or MLCT states. Strong σ-donating ligands, such as NHCs, present a suitable choice to push the dσ* orbital to a higher-lying energy.[131] In this context, the first luminescent gold(III) complex containing NHC ligands was reported by Yam and coworkers in 2009, with the synthesis of complexes **134-138** by direct incorporation of carbene ligands into Au(III) starting materials (Fig. 57).[132] All complexes exhibited a vibronic-structured band at 370-410 nm, which was assigned to a metal-perturbed π→π* IL transition of the RC^N^CR ligand, with some mixture of charge transfer character from the phenyl moiety to the pyridyl unit. With the exception of mesityl-substituted complexes (**134b** and **135**), all complexes showed moderately intense luminescence in both CH_2Cl_2 at 298 K and in glassy solution (EtOH/MeOH/CH_2Cl_2) at 77 K in the range 470-563 nm. Surprisingly, the emission lifetime values at 77 K (396-531 μs) were at least 660 times larger than those found at room temperature (0.6-10.3 μs). These results together with the enhancement of the luminescent properties of the gold(III) species after incorporation of NHCs allowed these emissions to be assigned as originating from a metal-perturbed ^{3}[π→π*] (RC^N^CR) IL state.

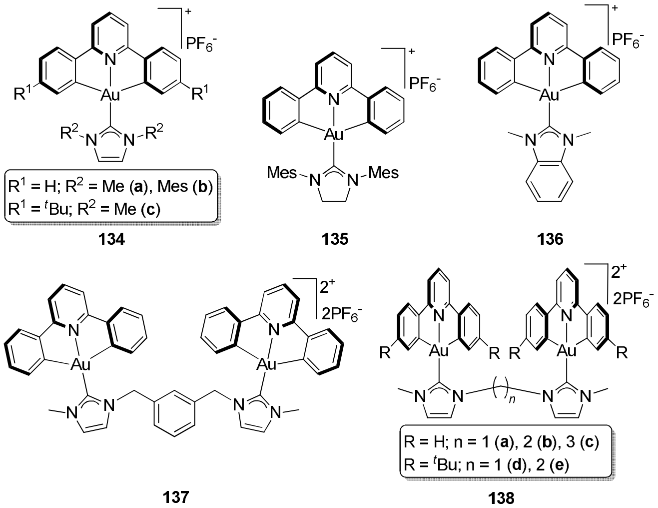


Fig. 57 First cyclometallated gold(III)-NHC complexes reported.

It is well known that a great number of gold complexes have been used as therapeutic agents.[133] The analogy between square planar complexes of Pt(II) and Au(III) has attracted much attention in the past decades, and many efforts have been made to design d^8 metal complexes with anticancer properties. One of the main characteristics required is good solubility and stability in polar solvents. Using the same synthetic route as for the preparation of **134a**, Che and coworkers synthesised the luminescent cyclometallated gold(III) complexes **139** and **140**, which showed similar characteristics to those previously mentioned (Fig. 58).[134] As expected, the electronic absorption spectra of complexes **139** and **140** in CH_2Cl_2 resemble those found for complexes **134-138**, exhibiting an absorption band at ca. 320 nm and another vibronic-structured band at ca. 400 nm. Furthermore, emission maxima were observed in the range 475-490 nm upon excitation at ca. 360 nm in CH_2Cl_2, and with τ = 0.52-0.82 μs.

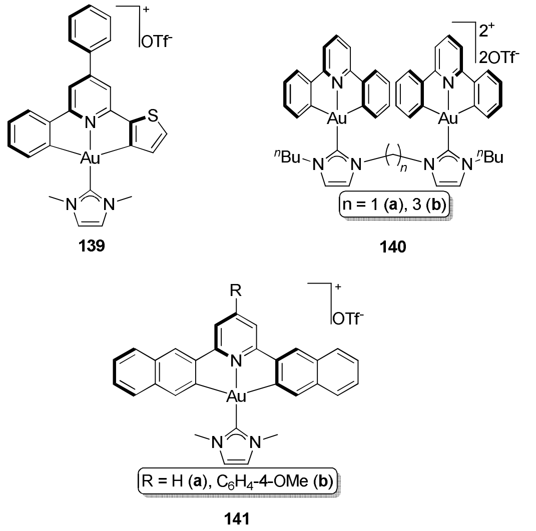


Fig. 58 Luminescent cyclometallated gold(III)-NHC complexes with anticancer and photocatalytic properties.

In their study, the authors also investigated the interaction of complex **134a**, using trifluoromethylsulfonate (OTf^-) as counterion instead of PF_6^-, with calf-thymus DNA in Tris-buffered saline, finding a pronounced increase in the intensity of the emission at 480 nm up to 5 times the original value. They also tested the DNA binding by UV-visible absorption titration. The electronic absorption spectra revealed spectral changes with isosbestic points at 323, 341 and 405 nm together with hyperchromicity (36%). All of the complexes showed inhibitory activity towards topoisomerase I, highlighting complex **134a·OTf**, which showed a prominent *in vitro* and *in vivo* anticancer activity, and induced DNA strand breaking and subsequent cell death.[134]

The photophysical and photocatalytic properties of complexes **141** were investigated by Che and coworkers (Fig. 58).[135] In this case, the presence of a π-extension was thought to enhance radiative decay by modification of the transition dipole and the oscillator strength of the $S_0 \rightarrow S_1$ transition, while suppressing nonradiative decay by decreasing the structural distortion in the first excited state. Thus, although emission profiles (λ_{em} = 520 nm) resemble those of cyclometallated organogold(III) complexes previously commented, complexes **141** exhibited high emission quantum yields and long-lived triplet excited states, reaching values of 506 and 282 μs in dichloromethane solutions and at room temperature. In addition, a great decrease of the emission intensity was observed after slow diffusion of air into a thoroughly degassed solution, and only 1% of emission intensity at 520 nm was retained. The photophysical properties of complexes **141** rendered them perfect candidates for photocatalytic performance. Indeed, oxidation of secondary amines and oxidative cyanation of tertiary amines using **141a** as catalyst (0.15 mol%) under light irradiation at room temperature were carried out, exhibiting an excellent activity, with almost all entries reaching 100% conversion. Moreover, complex **141a** also catalysed the light-induced generation of hydrogen upon irradiation with sunlight of a three-component system in a degassed MeCN/H_2O mixture, achieving until 250 turnovers of hydrogen after 4 hours.

Luminescent three-coordinate gold(I)-NHC complexes

Gold(I) has a much greater tendency to form linear complexes than other isolectronic centres, such as platinum(0), silver(I) and mercury(II). This particular behaviour of gold is attributed to the relativistic effects, which entail a diminishing of the energy gap between 6s and 5d orbitals, and consequently, a small difference of energy among s, p and d states leading to the efficient formation of s/d or s/p hybridisations.[136] The synthesis and characterisation of new three-coordinate gold(I) species has attracted particular attention, not only for the novel structural and geometrical situation, but also because of the luminescent properties that they normally possess, which are associated to a phosphorescent excited state whose structure is derived from a Jahn-Teller distortion towards a T-shape.[137] Very recently, we reported the first three-coordinate gold(I)-NHC complexes (**142**[138] and **143**[139]) which were easily synthesised from the corresponding [AuCl(NHC)] and bis-phosphine precursors (Fig. 59). Neutral derivatives (**142**) were conveniently characterised by NMR and X-ray diffraction analysis, confirming good stability in solution and solid state. The electronic absorption spectra of all complexes were featureless, exhibiting a single absorption band between 300-310 nm, which was associated to IL transitions. Surprisingly, upon excitation at 370 nm, an intense blue-green emission in solid state appeared, strongly dependent on the NHC used, and a modulation of the luminescence from 470 nm (**142d**) to 520 nm (**142b**) was observed. On the other hand, a moderate bathochromic shift was observed in degassed dichloromethane at room temperature, which was attributed to an increase of the polarity of the molecules in the excited state. Interestingly, solid samples of **142** showed very high quantum yield values, especially for **142b**, which reached almost 100%, and with emission lifetimes in the range of 10.9-21.8 μs. This remarkable influence of the NHC ligands on the optical properties of complexes **142** was corroborated by DFT and TD-DFT calculations, which showed that the HOMO was mainly composed of the delocalised orbitals on the *nido*-carborane and in the Au-C_{carb} bond, while the LUMO was predominantly located at the gold centre with further contributions from the carbene ligand. These observations allowed us to assign the phosphorescent emissions as derived from LML′CT transitions.

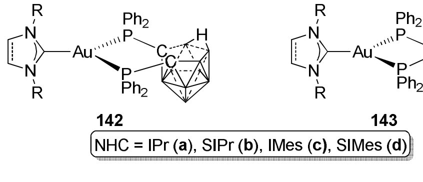


Fig. 59 Neutral and cationic three-coordinate Au(I)-NHC complexes.

Encouraged by the unique luminescent properties of complexes **142**, we aimed to synthesise cationic three-coordinate gold(I)-NHC complexes by using different chelating phosphines. The tendency of gold(I) to form linear complexes was reflected in attempts to prepare the desired species from flexible bisphosphines, where only the two-coordinate derivatives were obtained. It was necessary to incorporate a more rigid chelating ligand such as 1,2-bis-diphenylphosphine-benzene, which has a similar bite angle to that of diphosphine carborane, to achieve the cationic three-coordinate species **143** (Fig. 59).[139] Likewise, a modulation of the luminescence was observed, but in this case, the emissions were red-shifted (490-545 nm) compared to those found for **143**. A good illustration of this effect is depicted in Fig. 54.

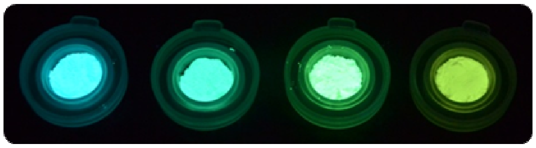


Fig. 60 Complexes **143b**, **143a**, **143c** and **143d** under UV light at 350 nm.

Again, the emission lifetimes were found in the range of 10.2-78.0 μs, and remarkable quantum yields with Φ = 80, 98 and 99% for **143a-143c**, respectively. Unfortunately, these efficiencies were considerably reduced in solution, showing quantum yields between 1.2-1.9%, and completely disappeared for the linear complexes. The straightforward synthesis of this new class of strongly luminescent complexes, accompanied by the facile access to the precursors,[140,141] opens new possibilities for the achievement of gold(I) materials suitable for future applications. The versatility of the NHC ligands offers new opportunities for the design of analogous complexes, and consequently, the controlled modification of their optical properties.

Conclusions and outlook

The synthesis of emissive transition metal complexes containing *N*-heterocyclic carbene ligands has experienced a substantial growth during the last few years. Groups 7-10 form numerous luminescent complexes based on conjugated chelating ligands, mainly cyclometallated species with pyridine and phenyl fragments. Combination of both cyclometallated and strongly σ-donating carbon ligands such NHCs ensures strong ligand fields with high lying d-d excited states. Thus, non-radiative deactivation from these states can be inhibited to a significant extent. This is important for group 11 metal complexes, especially for gold(III), where the use of strong donating ligands is essential. For the oxidation state M(I) the presence of emissive compounds requires the use of either chromophore groups, the formation of metallophilic interactions or changes in the geometry of the complexes, as seen for the tri-coordinate gold(I) derivatives.

The great versatility of NHC ligands for structural modifications, together with the presence of other ancillary ligands that can be modified in the molecule, opens a huge range of possibilities in the synthesis of phosphorescent materials with emission colours over the entire visible spectrum. These materials are of great interest in the preparation of OLEDs and subsequent use in flat panel displays and solid state lighting sources. For such applications three-colour white OLEDs are needed to generate a satisfying colour-rendering index (CRI). This is possible by the use of highly efficient deep blue, green and red phosphors with high quantum yields and very short luminescence decays (<5 μs). The majority of OLED devices contain organic molecules doped with phosphorescent iridium or platinum derivatives, and until now they have presented the best characteristics for the use in these devices.

Apart from use in OLEDs, these phosphorescent transition metal complexes containing NHC ligands may also be suitable for other applications such as biological labelling agents (mainly rhenium and ruthenium derivatives), charge-transfer reactions in DNA, antitumoral agents (gold and platinum complexes), phosphorescent sensors, photocatalysis for CO_2 reduction and photochemical water splitting.

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Notes and references

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1 L. Mercs and M. Albrecht, *Chem. Soc. Rev.*, 2010, **39**, 1903.

2 S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.

3 Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126.

4 J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561.

5 H. Yersin. Highly Efficient OLEDs with Phosphorescent Materials, WILEY-VCH, Weinheim, 2008.

6 R. C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093.

7 K. K.-W. Lo, K. Y. Zhang and S. P.-Y. Li, *Pure Appl. Chem.*, 2011, **83**, 823.

8 Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2007, **36**, 1421.

9 V. Fernández-Moreira, F. L. Thorp-Greenwood and M. P. Coogan, *Chem. Commun.*, 2010, **46**, 186.

10 F. Shao and J. K. Barton, *J. Am. Chem. Soc.*, 2007, **129**, 14733.

11 C.-M. Che and S.-W. Lai, Luminescence and Photophysics of Gold Complexes, 249, in “Gold Chemistry. Applications and Future Directions in the Life Science” Ed. F. Mohr, Wiley-VCH Verlag, 2008.

12 D.-L Ma and C.-M. Che, *Chem. Eur. J.*, 2003, **9**, 6133.

13 Y. You and S. Y. Park, *Adv. Mater.*, 2008, **20**, 3820.

14 K. A. Belmore, R. A. Vanderpool, J.-C. Tsai, M. A. Khan and K. M. Nicholas, *J. Am. Chem. Soc.*, 1988, **110**, 2004.

15 M. S. Lowry and S. Bernhard, *Chem. Eur. J.*, 2006, **12**, 7970.

16 M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712.
17 S. J. Hock, L. A. Schaper, W. A. Herrmann and F. E. Kühn, *Chem. Soc. Rev.*, 2013, **42**, 5073.
18 W.-M. Xue, M. C.-W. Chan, Z.-M. Su, K.-K. Cheung, S.-T. Liu and C.-M. Che, *Organometallics*, 1998, **17**, 1622.
19 L. A. Casson, S. Muzzioli, P. Raiteri, B. W. Skelton, S. Stagni, M. Massi and D. H. Brown, *Dalton Trans.*, 2011, **40**, 11960.
20 J. G. Vaughan, B. L. Reid, S. Ramchandani, P. J. Wright, S. Muzzioli, B. W. Skelton, P. Raiteri, D. H. Brown, S. Stagni and M. Massi, *Dalton Trans.*, 2013, **42**, 14100.
21 X.-W. Li, H.-Y. Li, G.-F. Wang, F. Chen, Y.-Z. Li, X.-T. Chen, Y.-X. Zheng and Z.-L. Xue, *Organometallics*, 2012, **31**, 3829.
22 G.-F. Wanga, Y.-Z. Liu, X.-T. Chen, Y.-X. Zheng, Z.-L. Xue, *Inorg. Chim. Acta*, 2013, **394**, 488.
23 S. U. Son, K. H. Park, Y.-S. Lee, B. Y. Kim, C. H. Choi, M. S. Lah, Y. H. Jang, D.-J. Jang and Y. K. Chung, *Inorg. Chem.*, 2004, **43**, 6896.
24 G. Duan and V. W.-W. Yam, *Chem. Eur. J.*, 2010, **16**, 12642.
25 B. Schulze, D. Escudero, C. Friebe, R. Siebert, H. Görls, U. Köhn, E. Altuntas, A. Baumgaertel, M. D. Hager, A. Winter, B. Dietzek, J. Popp, L. González, and U. S. Schubert, *Chem. Eur. J.*, 2011, **17**, 5494.
26 D. G. Brown, N. Sanguantrakun, B. Schulze, U. S. Schubert and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2012, **134**, 12354.
27 J. Dinda, S. Liatard, J. Chauvin, D. Jouvenot and F. Loiseau, *Dalton Trans.*, 2011, **40**, 3683.
28 V. Friese, S. Nag, J. Wang, M.-P. Santoni, A. Rodrigue-Witchel, G. S. Hanan and F. Schaper, *Eur. J. Inorg. Chem.*, 2011, 39.
29 H.-J. Park and Y. K. Chung, *Dalton Trans.*, 2012, **41**, 5678.
30 C.-S. Lee, R. R. Zhuang, J.-C. Wang, W.-S. Hwang and I. J. B. Lin, *Organometallics*, 2012, **31**, 4980.
31 V. Leigh, W. Ghattas, R. Lalrempuia, H. Mu□ller-Bunz, M. T. Pryce and M. Albrecht, *Inorg. Chem.*, 2013, **52**, 5395.
32 G. J. Barbante, P. S. Francis, C. F. Hogan, P. R. Kheradmand, D. J. D. Wilson and P. J. Barnard, *Inorg. Chem.*, 2013, **52**, 7448.
33 N. Robertson, *Angew. Chem. Int. Ed.*, 2006, **45**, 2338.
34 H.-J. Park, K. H. Kim, S. Y. Choi, H.-M. Kim, W. I Lee, Y. K. Kang and Y. K. Chung, *Inorg. Chem.*, 2010, **49**, 7340.
35 W.-C. Chang, H.-S. Chen, T.-Y. Li, N.-M. Hsu, Y. S. Tingare, C.-Y. Li, Y.-C. Liu, C. Su and W.-R. Li, *Angew. Chem. Int. Ed.*, 2010, **49**, 8161.
36 H.-S. Chen, W.-C. Chang, C. Su, T.-Y. Li, N.-M. Hsu, Y. S. Tingare, C.-Y. Li, J.-H. Shieb and W.-R. Li, *Dalton Trans.*, 2011, **40**, 6765.
37 L.-H. Chung, S.-C. Chan, W.-C. Lee and C.-Y. Wong, *Inorg. Chem.*, 2012, **51**, 8693.
38 L.-H. Chung, K.-S. Cho, J. England, S.-C. Chan, K. Wieghardt and C.-Y. Wong, *Inorg. Chem.*, 2013, **52**, 9885.
39 J.-Y. Tsai, US20120212125A1, 2012.
40 J.-Y. Tsai, US20120215000A1, 2012.
41 D. Tapu, C. Owens, D. VanDerveer and K. Gwaltney, *Organometallics*, 2009, **28**, 270.
42 H.-J. Park and Y. K. Chung, *Inorg. Chim. Acta*, 2012, **391**, 105.
43 T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 7992.
44 C.-H. Chien, S. Fujita, S. Yamoto, T. Hara, T. Yamagata, M. Watanabe and K. Mashima, *Dalton Trans.*, 2008, 916.
45 R. J. Holmes, S. R. Forrest, T. Sajoto, A. Tamayo, P. I. Djurovich, M. E. Thompson, J. Brooks, Y.-J. Tung, B. W. D'Andrade, M. S. Weaver, R. C. Kwong and J. J. Brown, *App. Phy. Lett.*, 2005, **87**, 243507.
46 N. Darmawan, C.-H. Yang, M. Mauro, M. Raynal, S. Heun, J. Pan, H. Buchholz, P. Braunstein and L. De Cola, *Inorg. Chem.*, 2013, **52**, 10756.
47 C.-H. Yang, J. Beltran, V. Lemaur, J. Cornil, D. Hartmann, W. Sarfert, R. Fröhlich, C. Bizzarri and L. De Cola, *Inorg. Chem.*, 2010, **49**, 9891.
48 F. Zhang, L. Duan, J. Qiao, G. Dong, L. Wang and Y. Qiu, *Org. Electr.*, 2012, **13**, 1277.
49 F. Monti, F. Kessler, M. Delgado, J. Frey, F. Bazzanini, G. Accorsi, N. Armaroli, H. J. Bolink, E. Ortí, R. Scopelliti, M. K. Nazeeruddin and E. Baranoff, *Inorg. Chem.*, 2013, **52**, 10292.
50 B. Wiegmann, P. G. Jones, G. Wagenblast, C. Lennartz, I. Münster, S. Metz, W. Kowalsky and H.-H. Johannes, *Organometallics*, 2012, **31**, 5223.
51 A. G. Tennyson, E. L. Rosen, M. S. Collins, V. M. Lynch and C. W. Bielawski, *Inorg. Chem.*, 2009, **48**, 6924.
52 C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang and C.-C. Wu, *Angew. Chem. Int. Ed.*, 2008, **47**, 4542.
53 C.-H. Hsieh, F.-I. Wu, C.-H. Fan, M.-J. Huang, K.-Y. Lu, P.-Y. Chou, Y.-H. O. Yang, S.-H. Wu, I.-C. Chen, S.-H. Chou, K.-T. Wong and C.-H. Cheng, *Chem. Eur. J.*, 2011, **17**, 9180.
54 H. Sasabe, J.-I. Takamatsu, T. Motoyama, S. Watanabe, G. Wagenblast, N. Langer, O. Molt, E. Fuchs, C. Lennartz and J. Kido, *Adv. Mater.*, 2010, **22**, 5003.
55 K.-T. Lu, H.-H. Chou, C.-H. Hsieh, Y.-H. O. Yang, H.-R. Tsai, H.-Y. Tsai, L.-C. Hsum C.-Y. Chen, I.-C. Chen and C.-H. Cheng, *Adv. Mater.*, 2011, **23**, 4933.
56 Y. Zhou, J. Jia, W. Li, H. Fei and M. Zhou, *Chem. Commun.*, 2013, **49**, 3230.
57 H. Kunkely A. Vogler, *J. Organomet. Chem.*, 2003, **684**, 113.
58 Q.-X. Liu, H.-B. Song, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng and Z.-Z. Zhang, *Polyhedron*, 2003, **22**, 1515.
59 Q.-X. Liu, F.-B. Xu, Q.-S. Li, H.-B. Song and Z.-Z. Zhang, *Organometallics*, 2004, **23**, 610.
60 H. Kunkely and A. Vogler, *J. Organomet. Chem.*, 2005, **690**, 6051.
61 T. Tsubomura, H. Murota and K. Takao, *Inorg. Chem. Commun.*, 3013, **35**, 110.
62 M. Koch, J. A. Garg, O. Blacque and K. Venkatesan, *J. Organomet. Chem.*, 2012, **700**, 154.
63 Y. Zhang, J. A. Garg, C. Michelin, T. Fox, O. Blacque and K. Venkatesan, *Inorg. Chem.*, 2011, **50**, 1220.
64 E. Chardon, G. Dahm, G. Guichard and S. Bellemin-Laponnaz, *Chem. Asian J.*, 2013, **8**, 1232.
65 Y. Unger, A. Zeller, S. Ahrens and T. Strassner, *Chem. Commun.*, 2008, 3263.
66 Y. Unger, A. Zeller, A. Taige and T. Strassner, *Dalton Trans.*, 2009, 4786.
67 Y. Unger, D. Meyer and T. Strassner, *Dalton Trans.*, 2010, **39**, 4295.

68 J. J. Hu, S.-Q. Bai, H. H. Yeh, D. J. Young, Y. Chi and T. S. A. Hor, *Dalton Trans.*, 2011, **40**, 4402.

69 T. Zou, C.-N, Lok, Y. M. E. Fung and C.-C. Che, *Chem. Commun.*, 2013, **49**, 5423.

70 H. Uesugi, T. Tsukuda, K. Takao and T. Tsubomura, *Dalton Trans.*, 2013, **42**, 7396.

71 M. Egen, K. Kahle, M. Bold, T. Gessner, C. Lennartz, S. Nord, H.-W. Schmidt, M. Thelakkat, M. Baete, C. Neuber, W. Kowalsky, C. Schildknecht and H.-H Johannes, WO2006056418A2, 2006.

72 N. Langer, K. Kahle, C. Lennartz, O. Molt, E. Fuchs, J. Rudolph, C. Schildknecht, S. Watanabe and G. Wagenblast, WO2009003898A1, 2009.

73 Y. Unger, D. Meyer, O. Molt, C. Schildknecht, I. Münster, G. Wagenblast and T. Strassner, *Angew. Chem. Int. Ed.*, 2010, **49**, 10214.

74 A. Tronnier and T. Strassner, *Dalton Trans.*, 2013, **42**, 9847.

75 Z. M. Hudson, C. sun, M. G. Helander, Y.-L. Chang, Z.-H. Lu and S. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 13930.

76 A. Tronnier, A. Rissler, N. Langer, G. Wagenblast, I. Münster and T. Strassner, *Organometallics*, 2012, **31**, 7447.

77 K. Li, X. Guan, C.-W. Ma, W. Lu, Y. Chen and C.-M. Che, *Chem. Commun.*, 2011, **47**, 9075.

78 K. Li, G. Cheng, C. Ma, X. Guan, W.-M. Kwok, Y. Chen, W. Lu, C.-M. Che. *Chem. Sci.*, 2013, **4**, 2630.

79 K. D. M. MaGee, P. J. Wright , S. Muzzioli, C. M. Siedlovskas, P. Raiteri, M. V. Baker, D. H. Brown, S. Tagni and M. Massi, *Dalton Trans.*, 2013, **42**, 4233.

80 K. Li, Y. Chen, W. Lu, N. Zhu and C.-M. Che, *Chem. Eur. J.*, 2011, **17**, 4109.

81 R. W.-Y. Sun, A. L.-F. Chow, X.-H. Li, J. J. Yan, S. S.-Y. Chui and C.-M. Che, *Chem. Sci.*, 2012, **2**, 728.

82 C.-S. Lee, S. Sabiah, J.-C. Wang, W.-S. Hwang and I. J. B. Lin, *Organometallics*, 2010, **29**, 286.

83 C.-S. Lee, R. R. Zhuang, S. Sabiah, J.-C. Wang, W.-S. Hwang and I. J. B. Lin, *Organometallics*, 2011, **30**, 3897.

84 S. Y.-L. Leung, E. S.-H. Lam, W. H. Lam, K. M.-C. Wong, W.-T. Wong and V. W.-W. Yam, *Chem. Eur. J.*, 2013, **19**, 10360.

85 X. Zhang, A. M. Wright, N. J. De Yonker, T. K. Hollis, N. I. Hammer, C. E. Webster and E. J. Valente, *Organometallics*, 2012, **31**, 1664.

86 T. K. Hollis and X. Zhang, WO2011050003A2, 2011.

87 X. Zhang, B. Cao, E. J. Valente and T. K. Hollis, *Organometallics*, 2013, **32**, 752.

88 A. J. Huckaba, B. Cao, T. K. Hollis, H. U. Valle, J. T. Kelly, N. I. Hammer, A. G. Oliver and C. E. Webster, *Dalton Trans.*, 2013, **42**, 8820.

89 H. M. J. Wang, C. Y. L. Chen and I. J. B. Lin, *Organometallics*, 1999, **18**, 1216.

90 K. Matsumoto, N. Matsumoto, A. Ishii, T. Tsukuda, M. Hasegawa and T. Tsubomura, *Dalton Trans.*, 2009, 6795.

91 V. A. Krylova, P. I. Djurovich, M. T. Whited and M. E. Thompson, *Chem. Commun.*, 2010, **46**, 6696.

92 V. A. Krylova, P. I. Djurovich, J. W. Aronson, R. Haiges, M. T. Whited and M. E. Thompson, *Organometallics*, 2012, **31**, 7983.

93 V. J. Catalano, L. B. Munro, C. E. Strasser and A. F. Samin, *Inorg. Chem.*, 2011, 50, 8465.

94 X. Zhang, S. Gu, Q. Xia and W. Chen, *J. Organomet. Chem.*, 2009, **694**, 2359.

95 A. Poethig and T. Strassner, *Organometallics*, 2011, **30**, 6674.

96 F. Cui, P. Yang, X. Huang, X.-J. Yang and B. Wu, *Organometallics*, 2012, **31**, 3512.

97 M. Kriechbaum, J. Ho□lbling, H.-G. Stammler, M. List, R. J. F. Berger and U. Monkowius, *Organometallics* 2013, **32**, 2876.

98 J. Wu, W. Liu, J. Ge, H. Zhang and P. Wang, *Chem. Soc. Rev.*, 2011, **40**, 3483.

99 Q.-X. Liu, Z.-Q. Yao, X.-J. Zhao, Z.-X. Zhao and X.-G. Wang, *Organometallics*, 2013, **32**, 3493.

100 S. D. Adhikary, L. Jhulki, S. Seth, A. Kundu, V. Bertolasi, P. Mitra, A. Mahapatra and J. Dinda, *Inorg. Chim. Acta*, 2012, **384**, 239.

101 S. D. Adhikary, S. K. Seth, M. R. Senapati and J. Dinda, *J. Mol. Struct.*, 2013, **1042**, 123.

102 V. W.-W. Yam, J. K.-W. Lee, C.-C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2009, **131**, 912.

103 M. Kriechbaum, M. List, R. J. F. Berger, M. Patzschke and U. Monkowius, *Chem. Eur. J.*, 2012, **18**, 5506.

104 J. Dinda, S. D. Adhikary, S. K. Seth and A. Mahapatra, *New J. Chem.*, 2013, **37**, 431.

105 C. Carcedo, J. C. Knight, S. J. A. Pope, I. A. Fallis and A. Dervisi, *Organometallics*, 2011, **30**, 2553.

106 M. C. Gimeno, A. Laguna and R. Visbal, *Organometallics*, 2012, **31**, 7146.

107 J. Carlos Lima and L. Rodríguez, *Chem. Soc. Rev.*, 2011, **40**, 5442.

108 A. L.-F. Chow, M.-H. So, W. Lu, N. Zhu and C.-M. Che, *Chem. Asian J.*, 2011, **6**, 544.

109 J. A. Garg, O. Blacque, J. Heier and K. Venkatesan, *Eur. J. Inorg. Chem.*, 2012, 1750.

110 L. Gao, D. V. Partyka, J. B. Updegraff III, N. Deligonul and T. G. Gray, *Eur. J. Inorg. Chem.*, 2009, 2711.

111 G. C. Fortman, A. Poater, J. W. Levell, S. Gaillard, A. M. Z. Slawin, I. D. W. Samuel, L. Cavallo and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 10382.

112 J. Gil-Rubio, V. Cámara, D. Bautista and J. Vicente, *Organometallics*, 2012, **31**, 5414.

113 D. V. Partyka, L. Gao, T. S. Teets, J. B. Updegraff III, N. Deligonul and T. G. Gray, *Organometallics*, 2009, **28**, 6171.

114 L. Gao, M. A. Peay, D. V. Partyka, J. B. Updegraff, T. S. Teets, A. J. Esswein, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2009, **28**, 5669.

115 J. Y. Z. Chiou, S. C. Luo, W. C. You, A. Bhattacharyya, C. S. Vasam, C. H. Huang and I. J. B. Lin, *Eur. J. Inorg. Chem.*, 2009, 1950.

116 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931.

117 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370.

118 V. J. Catalano, A. L. Moore, J. Shearer and J. Kim, *Inorg. Chem.*, 2009, **48**, 11362.

119 C. E. Strasser and V. J. Catalano, *J. Am. Chem. Soc.*, 2010, **132**, 10009.

120 V. J. Catalano and C. E. Strasser, US20130011926A1, 2013.

121 C. E. Strasser and V. J. Catalano, *Inorg. Chem.*, 2011, **50**, 11228.

122 A. K. Ghosh and V. J. Catalano, *Eur. J. Inorg. Chem.*, 2009, 1832.

123 O. Elbjeirami, M. D. Rashdan, V. Nesterov and M. A. Rawashdeh-Omary, *Dalton Trans.*, 2010, **39**, 9465.

124 A. Poethig and T. Strassner, *Organometallics*, 2012, **31**, 3431.

125 V. Gierz, A. Seyboldt, C. Maichle-Mo□ssmer, K. W. To□rnroos, M. T. Speidel, B. Speiser, K. Eichele and D. Kunz, *Organometallics*, 2012, **31**, 7893.

126 M. Baron, C. Tubaro, A. Biffis, M. Basato, C. Graiff, A. Poater, L. Cavallo, N. Armaroli and G. Accorsi, *Inorg. Chem.*, 2012, **51**, 1778.

127 C. Hemmert, R. Poteau, F. J.-B. dit Dominique, P. Ceroni, G. Bergamini and H. Gornitzka, *Eur. J. Inorg. Chem.*, 2012, 3892.

128 C. Tubaro, M. Baron, M. Costante, M. Basato, A. Biffis, A. Gennaro, A. A. Isse, C. Graiff and G. Accorsi, *Dalton Trans.*, 2013, **42**, 10952.

129 F. J.-B. dit Dominique, H. Gornitzka, A. Sournia-Saquet and C. Hemmert, *Dalton Trans.*, 2009, 340.

130 B. Ballarin, L. Busetto, M. C. Cassani, C. Femoni, A. M. Ferrari, I. Milettob and G. Caputo, *Dalton Trans.*, 2012, **41**, 2445.

131 C. Bronner and O. S. Wenger, *Dalton Trans.*, 2011, **40**, 12409.

132 V. K.-M. Au, K. M.-C. Wong, N. Zhu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2009, **131**, 9076.

133 C. F. Shaw, *Chem. Rev.*, 1999, **99**, 2589.

134 J. J. Yan, A. L.-F. Chow, C.-H. Leung, R. W.-Y. Sun, D.-L. Ma and C.-M. Che, *Chem. Commun.*, 2010, **46**, 3893.

135 W.-P. To, G. S.-M. Tong, W. Lu, C. Ma, J. Liu, A. L.-F. Chow and C.-M. Che, *Angew. Chem. Int. Ed.*, 2012, **51**, 2654.

136 M. C. Gimeno and A. Laguna, *Chem. Rev.*, 1997, **97**, 511.

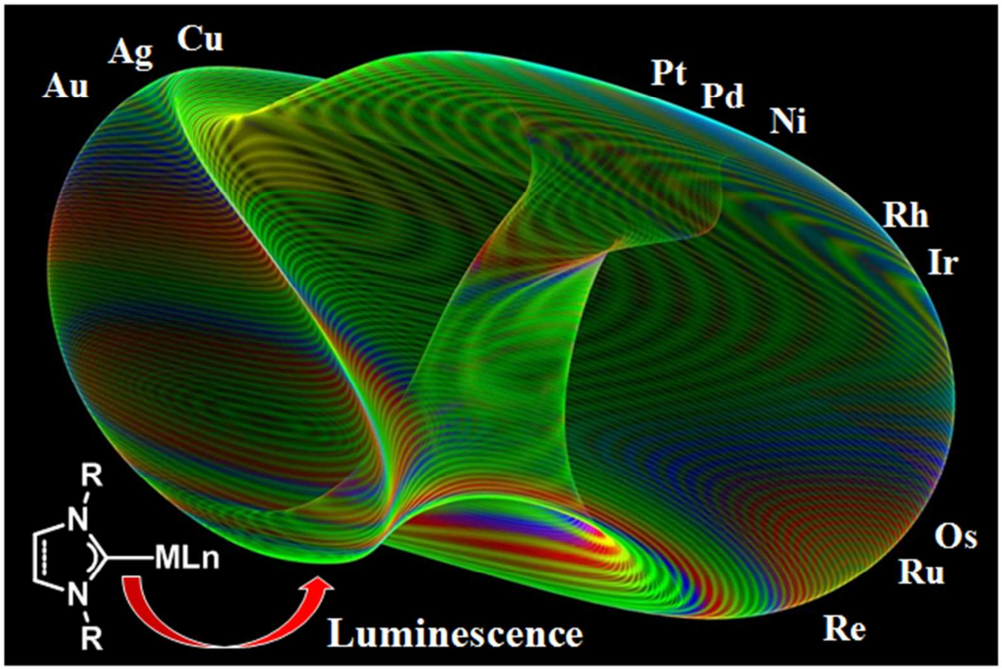
137 P. Sinha, A. K. Wilson and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 12488.

138 R. Visbal, I. Ospino, J. M. López-de-Luzuriaga, A. Laguna and M. C. Gimeno, *J. Am. Chem. Soc.*, 2013, **135**, 4712.

139 R. Visbal, J. M. López-de-Luzuriaga, A. Laguna and M. C. Gimeno, *Dalton Trans.*, 2014, **43**, 328.

140 R. Visbal, A. Laguna and M. C. Gimeno, *Chem. Commun.*, 2013, **49**, 5642.

141 A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun.*, 2013, **49**, 5541.



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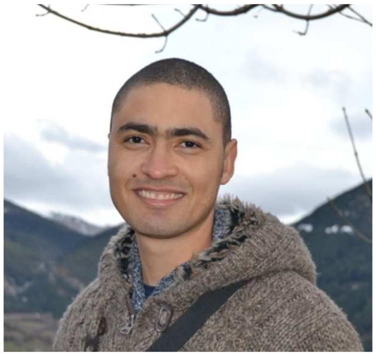

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