Dalton Transactions

PERSPECTIVE

Luminescent cyclometalated gold(III) complexes

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Many luminescent gold(I) compounds are known, but in the vast majority of gold(III) complexes reported until recently, room temperature emission in fluid solution does not occur. As for other d^8 and d^6 metals, the key to obtaining gold(III) compounds with favorable luminescence properties seems to be the use of cyclometalating ligands that ensure very strong ligand fields. Recent progress in this emerging research field is discussed, and where appropriate, comparison to isoelectronic platinum(II) complexes and their photophysical properties is made.

1. Introduction

Cyclometalated d^6 and d^8 complexes have been known for a very long time, but only rather recently did they experience a remarkable revival. This is illustrated by Fig. 1 which shows the numbers of publications that have appeared on the subjects of cyclometalated iridium, platinum, and gold over the past 30 years. Much of the recent work was driven by the motivation to use some of these complexes as luminophors in organic light emitting diodes (OLEDs).[1,2] Purely organic light emitters usually only fluoresce, and if triplet excitons are formed, they are simply turned into heat. However,

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with heavy-metal complexes that exhibit strong spin-orbit coupling and luminescence from triplet excited states, triplet excitons can be converted into light. Statistically, an electroluminescent device will form 25% singlet and 75% triplet excitons, hence the internal efficiency of an OLED can theoretically be improved by a factor of 4 when it is doped with emissive heavy-metal complexes. Aside from quantum efficiency, color tuning is an important issue for OLEDs.[1,3] Cyclometalated iridium(III) complexes turned out to be particularly attractive in this respect, because their emission colors can be tuned all the way from red to blue.[3–7] Analogies between the excited-state structures of these cyclometalated iridium(III) compounds with d^6 metal diimine complexes such as $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) did also make these complexes obvious targets for many photochemical investigations. To name a few examples, cyclometalated iridium(III) complexes were explored in the contexts of photochemical water splitting,[7,8]

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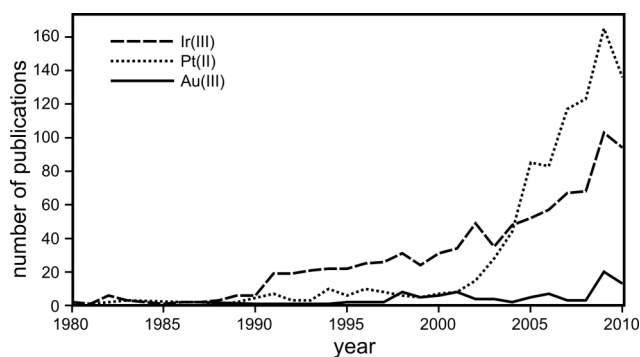
Fig. 1 Number of publications that have appeared on cyclometalated complexes of iridium(III), platinum(II), and gold(III) over the past 30 years. (ISI Web of Science search for "cyclomet* and irid*"; "cyclomet* and platin*"; "cyclomet* and gold").
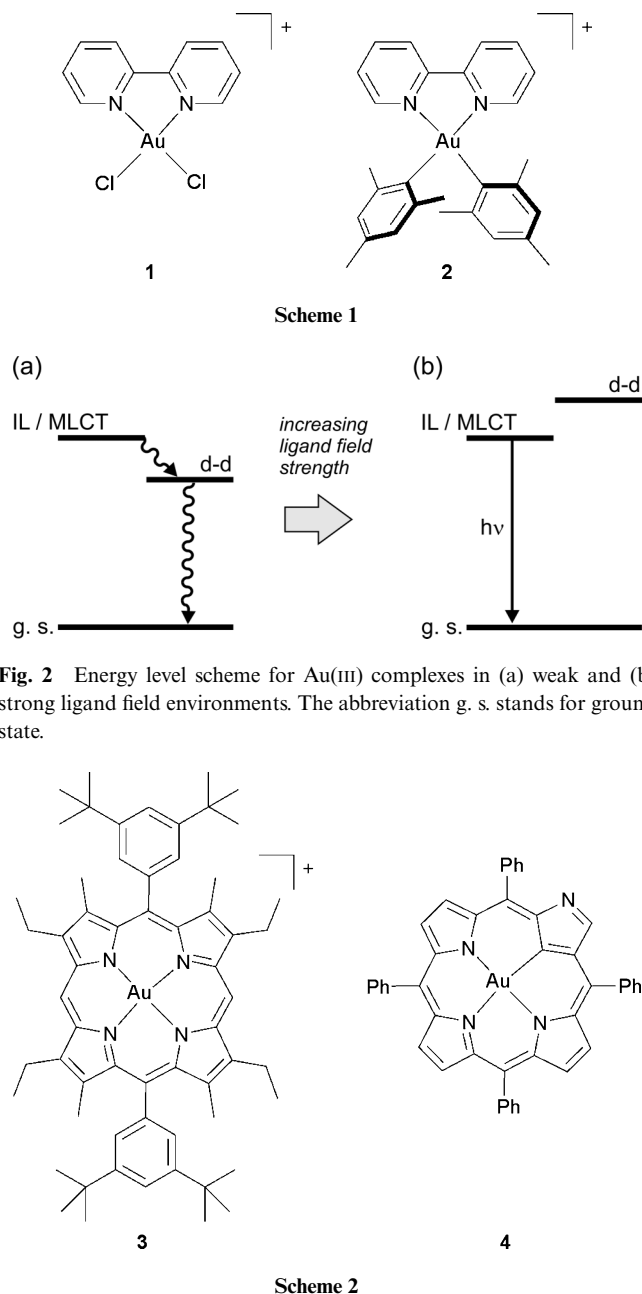
dye-sensitized solar cells,[9] long-range electron transfer,[10,11] and oxygen sensors.[7,12]

As seen from Fig. 1, research activity on cyclometalated platinum(II) complexes started to increase almost a decade later, but in the meantime these complexes are being explored even more intensely than cyclometalated iridium(III) compounds. By contrast, comparatively little research is still being performed on cyclometalated gold(III) complexes, but from Fig. 1 it becomes obvious that this field very recently experienced an increase in activity. This observation, combined with the promising results reported in many of the recent publications on the subject of luminescent cyclometalated gold(III) complexes, provided the motivation for this perspectives article. An excellent brief survey of gold(I) and gold(III) photophysics and photochemistry was given by Yam and Cheng in 2007,[13] but in the meantime many additional discoveries have been made, particularly regarding luminescent cyclometalated gold(III) complexes.

2. Factors governing nonradiative relaxation in square-planar Au(III) complexes

The majority of non-cyclometalated gold(III) complexes known to date do not emit in fluid solution at room temperature.[14] A representative example is the $[Au(bpy)Cl_2]^+$ complex (**1**) which emits in the solid state, but not in solution.[15] The same observation has been made for the isoelectronic $[Pt(bpy)Cl_2]$ species and for other square-planar $[Au(\alpha\text{-diimine})Cl_2]^+$ complexes.[16] However, when the chloro-ligands of **1** are substituted by mesityl-ligands, the resulting complex (**2**) is luminescent in acetonitrile solution at room temperature (Scheme 1).[15] Nonradiative excited-state deactivation in **1** and related complexes is thought to involve d–d states that are energetically close to potentially emissive intraligand (IL) or metal-to-ligand charge transfer (MLCT) states (Fig. 2a).[16] The mesityl-ligands are strong σ-donors, and this is expected to lead to an increase of the ligand field strength, which in turn decreases the probability for thermal population of non-emissive d–d states (Fig. 2b).

Analogous observations have been made for Au(III) porphyrin systems. Contrary to other metalloporphyrins, ordinary gold(III) porphyrin systems such as molecule **3** (Scheme 2) are essentially non-luminescent in fluid solution at room temperature.[17,18] In frozen glass matrices at temperatures below 200 K there is
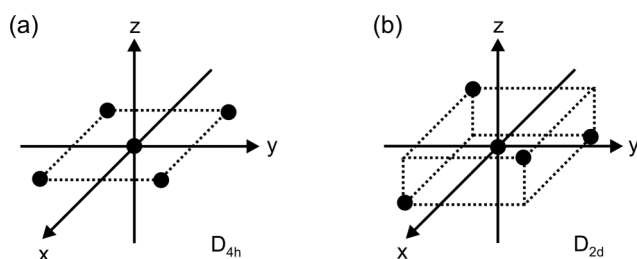

Scheme 1

Fig. 2 Energy level scheme for Au(III) complexes in (a) weak and (b) strong ligand field environments. The abbreviation g. s. stands for ground state.

Scheme 2

phosphorescence, which occurs with lifetimes on the order of 50–200 μs and quantum yields around 0.005. At room temperature, intersystem crossing from the initially excited singlet state to the corresponding triplet state was found to occur within less than a picosecond, and nonradiative deactivation of the latter takes place on the order of about a nanosecond. There is evidence for the involvement of ligand-to-metal charge transfer (LMCT) states in the emission quenching process.

A recent study reports on gold(III) in N-confused tetraphenyl-porphyrin (**4**) (Scheme 2) in which one of the pyrrole rings ligates to the metal center with a carbon atom.[19] This complex is emissive in solution at ambient temperature. The luminescence quantum yield is on the order of 2×10^{-4}, and the emission decays within nanoseconds. Despite the short lifetime, this emission was attributed to phosphorescence because of its large Stokes shift (~3000 cm^{-1}). Be that as it may, the comparison of the ordinary

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porphyrin, **3**, and its organometallic analogue, **4**, shows that the presence of a strongly σ-donating ligand atom is beneficial for the luminescence properties.

Many square-planar d[8] complexes are unstable with respect to molecular distortions that lead to a symmetry decrease from D_{4h} to D_{2d} (Fig. 3),[20] and this is known to facilitate nonradiative excited-state decay.[21] A common strategy to avoid this problem is the use of tridentate rather than bidentate chelating ligands.[1] Complex **5** with its 4′-(4-methoxyphenyl)-tpy ligand (tpy = 2,2′;6′,2″-terpyridine) is one of the very rare examples of a gold(III) polypyridine complex that is emissive in fluid solution at room temperature.[22] It exhibits IL luminescence at 480 nm with a lifetime of 0.25 µs in a methanol-Tris buffer solution from which it can bind to DNA. Its cyclometalated analogue (**6**) emits at a longer wavelength (530 nm) and with a lifetime almost twice as long (Scheme 3).

Fig. 3 Distortion of square planar complexes from D_{4h} to D_{2d} symmetry. Adapted with permission from Ref. 20 Copyright 1965 American Chemical Society.
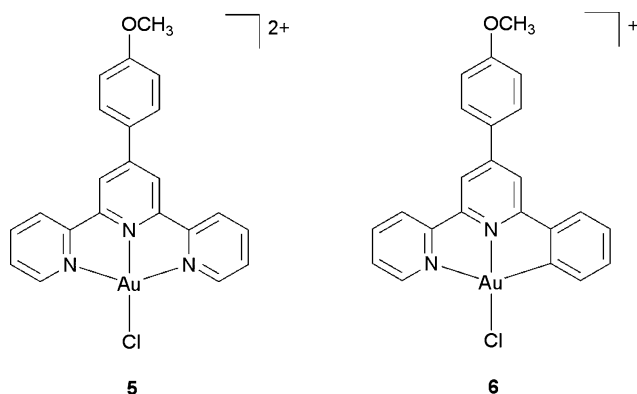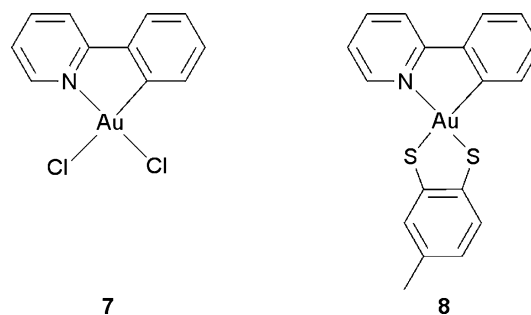

Scheme 3

Taken together, these results indicate that the experimentalist has two essential control parameters to obtain luminescent (square-planar) gold(III) complexes: the ligand field strength and the rigidity of the chelating ligands.

## 3. Complexes with bidentate C^N ligands

In the course of their research on platinum(II) thiolate complexes, Eisenberg and co-workers also reported on Au(III) thiolate complexes with 2-phenylpyridine as a bidentate cyclometalating ligand.[23] Complex **8** was obtained from a dichloro-precursor, **7**, as a mixture of *cisoid* and *transoid* forms (Scheme 4). Due to its planar structure, dithiolate **8** can adopt a solid-state structure with individual complexes stacked on top of each other, but the
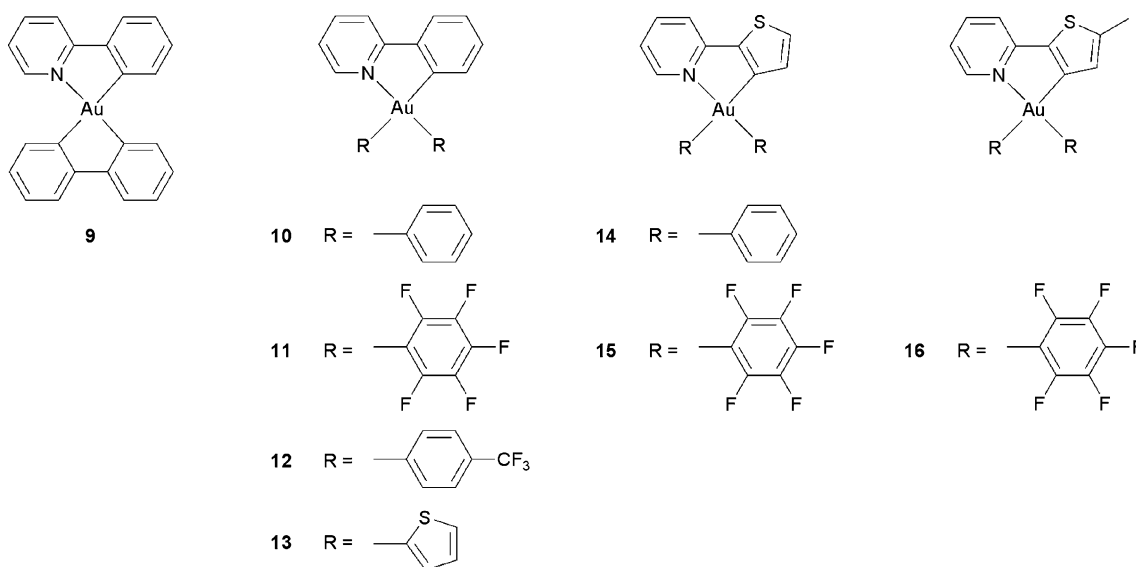

Scheme 4

shortest Au(III)–Au(III) distance is 3.60 Å, which is too long to indicate any significant attraction between individual metal centers. Complex **8** is emissive neither in fluid solution at room temperature nor at 77 K. This observation is somewhat striking because of the fact that Pt(II) diimine dithiolate complexes are luminescent under these conditions. In these platinum complexes, the lowest excited state involves an electronic transition from a mixed metal–dithiolate orbital to a diimine π* orbital. The absence of emission in the Au(III) complex **8** suggests that the nature of the lowest excited state is different in this case. Energetically low-lying d–d and LMCT transitions have been discussed as possible reasons for emission quenching, but at this point the electronic structure of complex **8** and related Au(III) compounds does not appear to be understood sufficiently well to permit a definitive conclusion.

In very recent work by Venkatesan and co-workers, complex **7** served as a precursor for the synthesis of several charge-neutral Au(III)-complexes (**9–13**) (Scheme 5), all of which are luminescent in room temperature solution and in frozen glasses at 77 K.[24] Their absorption and emission spectra are virtually identically to each other (Fig. 4). Vibrational progressions in a ~1500 cm^{−1} mode, discernable already in the room-temperature emission spectra, are consistent with coupling of the luminescence transition to breathing modes of the aromatic ligands. Luminescence lifetimes vary between 0.33 and 4.41 µs at 298 K. Taken together, these observations indicate that emission occurs from a metal-perturbed [3]IL state.
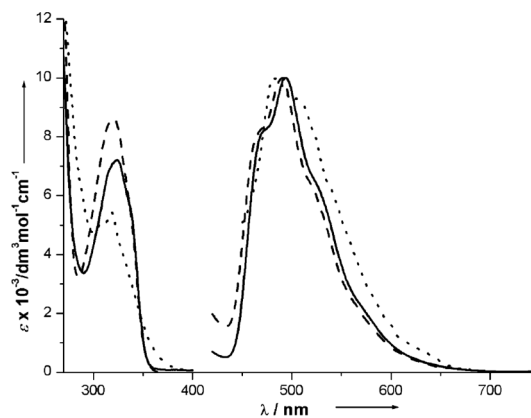
Fig. 4 Optical absorption (left) and (normalized) luminescence spectra (right) of complexes **9** (dotted), **10** (dashed), **11** (solid) in dichloromethane solution at room temperature. Adapted with permission from Ref. 24 Copyright 2010 American Chemical Society.
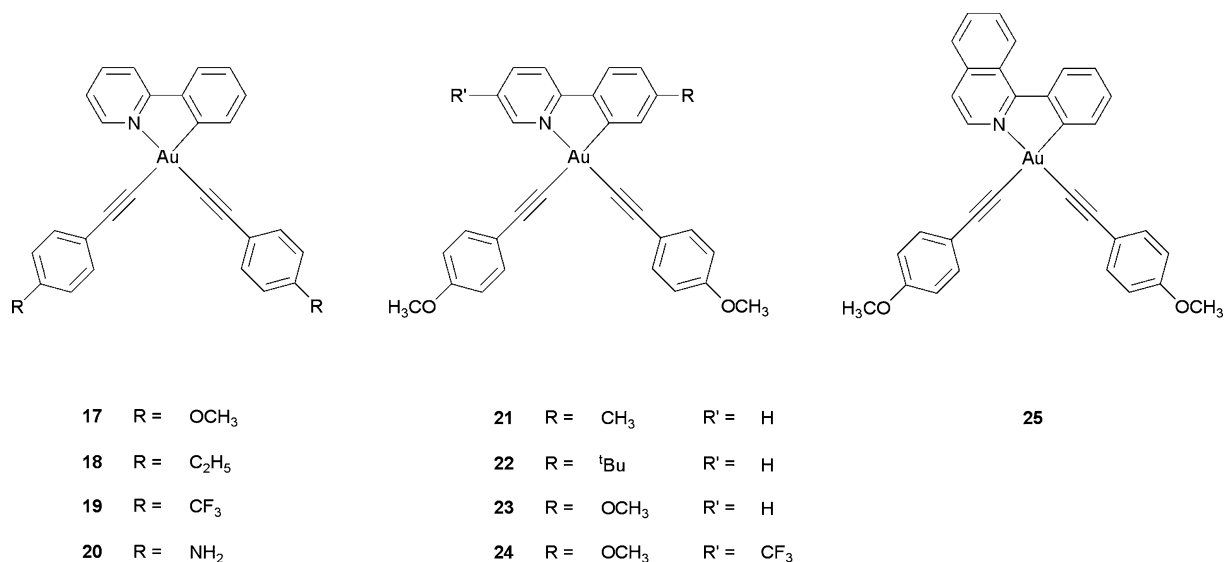
Scheme 5

Upon replacement of 2-phenylpyridine by a 2-(2-thienyl)-pyridine ligand (complexes **14–16**) (Scheme 5), the emission shifts to lower energies by almost 2000 cm^{-1}.[24] Interestingly, this red-shift is neither accompanied by a decrease in luminescence lifetime, nor in luminescence quantum yield, contrary to what is frequently observed for d^6 metal diimines which follow the so-called energy gap law.[25] DFT calculations show that the frontier orbitals are essentially entirely located on the bidendate cyclometalating (C^N) ligands, and thus support the assignment of the luminescence to a π–π* transition. Fluoro-substitution of the ligands ancillary to the C^N chelates has a much larger impact on the chemical stability of these Au(III) complexes than on their photophysical properties: Perfluorinated ligands (**11**, **15**, **16**) appear to yield stable complexes, while others were reported to show signs of decomposition over time.

Concentration-dependent UV-Vis absorption studies revealed no deviations from the Lambert–Beer law, and X-ray crystallographic investigations exhibited no Au–Au distances shorter than 4.80 Å.[24] Thus, there is no evidence for significant metal–metal interactions, neither in solution nor in the solid state.

Again starting from dichloro-complex **7**, Yam and coworkers synthesized a series of dialkynylgold(III) complexes (**17–20**) (Scheme 6) with favorable luminescence properties.[26] In this instance, a significantly larger tunability of the luminescence band maximum (λ_{em}) is possible: With the methoxy- and ethyl-substituted phenylacetylide ligands λ_{em} is at ~492 nm (**17**, **18**), while for the amino-substituted system (**20**) it is at 613 nm. In the case of complexes **17–19**, emission was attributed to ^{3}IL luminescence, based on essentially the same arguments used above for complexes **9–16**. In complex **20**, with the electron-rich amino-group attached


17	R =	OCH$_3$
18	R =	C$_2$H$_5$
19	R =	CF$_3$
20	R =	NH$_2$

21	R =	CH$_3$	R' =	H
22	R =	^{t}Bu	R' =	H
23	R =	OCH$_3$	R' =	H
24	R =	OCH$_3$	R' =	CF$_3$

25

Scheme 6

to the phenylacetylide ligand, the rather broad and structureless 613 nm emission was attributed to a ligand-to-ligand charge transfer (LLCT) state involving an electronic transition from the aminophenyl-alkynyl group to a π^* orbital of phenylpyridine.

Some emission color tuning is possible through the introduction of chemical substituents at the C^N ligand.[26] Complex **17** as well as complexes **21–23** (Scheme 6) have identical methoxy-phenylacetylide ancillary ligands, but different electron-donating groups are attached to the phenyl-ring of the cyclometalating ligand. Experimentally, this is found to lead to a red-shift of λ_{em} from 492 nm to 514 nm between complex **17** and complex **23**, which signals a decrease of the HOMO–LUMO gap. Attachment of electron-withdrawing groups to the pyridine-ring of the C^N ligand has qualitatively the same effect: Complexes **23** and **24** differ only by a trifluoromethyl group at the pyridine ring, and this leads to a shift of λ_{em} from 514 nm to 523 nm (Scheme 6).

Replacement of the pyridine-ring in the cyclometalating ligand by an isoquinoline group entails a red-shift from 492 nm for complex **17** to 621 nm for complex **25**, reflecting the increased extent of π-delocalization in the larger aromatic system.[26]

Nanosecond pump–probe spectroscopy on complex **17** revealed the existence of transient absorption bands in the 350–600 nm wavelength range with a lifetime different from that of the luminescent excited state of this complex (Fig. 5).[26] Some of the observed spectral features resemble those previously reported for reduced 2-phenylpyridine, while others are similar to the spectroscopic signatures of oxidized di- and trimethoxybenzenes. On these grounds, the long-lived spectral features were attributed to a charge-separated state with an electron located on the phenylpyridine ligand and a hole located on a methoxy-substituted phenylacetylide unit. Similar observations were made for complex **20**. The lifetimes of the charge-separated states in these complexes are on the order of 0.5 µs, which is remarkably long, given the relatively short distance between the donor and acceptor moieties.
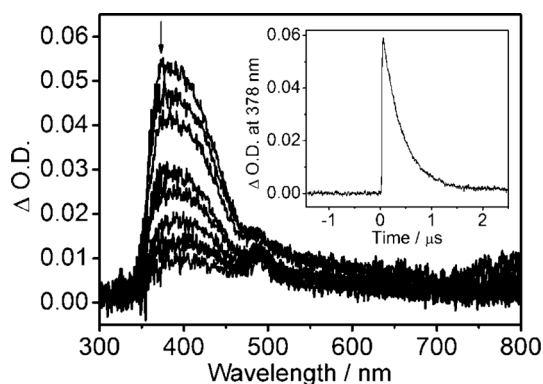

Fig. 5 Transient absorption spectra of complex **17** (in CH₂Cl₂ at 298 K) measured in 0.1 µs time intervals between 0 and 0.8 µs after excitation. The inset shows the temporal evolution of the transient absorption intensity at 378 nm. (Ref. 26 Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

4. Complexes with tridentate C^N^N and C^N^C ligands

One of the earliest reports on a luminescent Au(III) complex with a tridentate cyclometalating ligand is from Che and coworkers

and dates from 1994.[27] In this work, complex **26** (Scheme 7) was found to be emissive in fluid solution at room temperature. The occurrence of a vibrational progression in the emission spectrum, its Stokes shift, and the luminescence lifetime (~0.5 µs) point to a metal-perturbed ³IL state as the lowest-lying excited state in this case as well. A particularly interesting aspect of complex **26** is its photoredox behavior: Cyclic voltammetry shows that this complex is reduced at −0.84 V vs. Fc⁺/Fc, and given an excited-state energy of 2.38 eV, one arrives at an estimate of 2.2 V vs. NHE for the excited-state reduction potential of **26**. Indeed, when complex **26** is mixed with 1,4-dimethoxybenzene in 1 : 100 ratio in acetonitrile solution, excitation of the gold(III) complex leads to the formation of 1,4-dimethoxybenzene radical cations as demonstrated by transient absorption spectroscopy. Moreover, complex **26** appears to be able to induce oxidative ring cleavage of tetrahydrofuran solvent molecules. These two observations demonstrate that complex **26** is an unusually powerful photooxidant. However, after prolonged irradiation, there is also evidence for the formation of colloidal gold, and it thus appears that photoreduction of complex **26** is not an equally reversible process as in many other d⁸ and d⁶ metal systems.
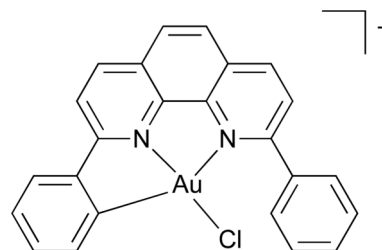

26

Scheme 7

The first Au(III) complexes with the tridentate 2,6-diphenylpyridine ligand were reported by Che and coworkers in 1998.[28] As part of an effort toward the development of cyclometalated binuclear d⁸–d⁸ complexes with face-to-face arrangement, chloro-complex **27** and three other mononuclear Au(III) compounds with the same C^N^C ligand were synthesized and found to be luminescent at 77 K but not at room temperature. Comparison of their emission spectra to those of the free 2,6-diphenylpyridine ligand indicates that their low-temperature emissions are due to a metal-perturbed ³IL state, and the observation of vibrational fine structure in regular energy intervals of 1100–1300 cm⁻¹ is in line with this interpretation.

As for isoelectronic Pt(II) species, bis(diphenylphosphino)-methane (μ-dppm) can act as a bridging ligand between two [Au(III)(C^N^C)]⁺ units, thereby yielding complex **28** (Scheme 8).[28] However, the intramolecular Au(III)–Au(III) distance determined from a crystal structure analysis of this binuclear complex is 3.4 Å, which is slightly above the upper limit of what would be typical for significant Au–Au interactions. The maximum of the emission band of **28** is red-shifted by ~1600 cm⁻¹ with respect to λ_{em} of complex **27** and its other mononuclear congeners. This is typical behavior for metal-metal-to-ligand charge transfer (MMLCT) transitions that emerge from mutual interactions between Pt(II) or other d⁸ metal centers.[29,30] However, given the comparatively
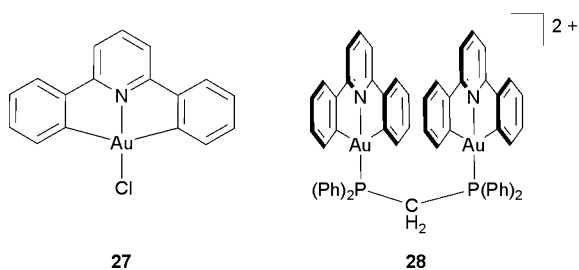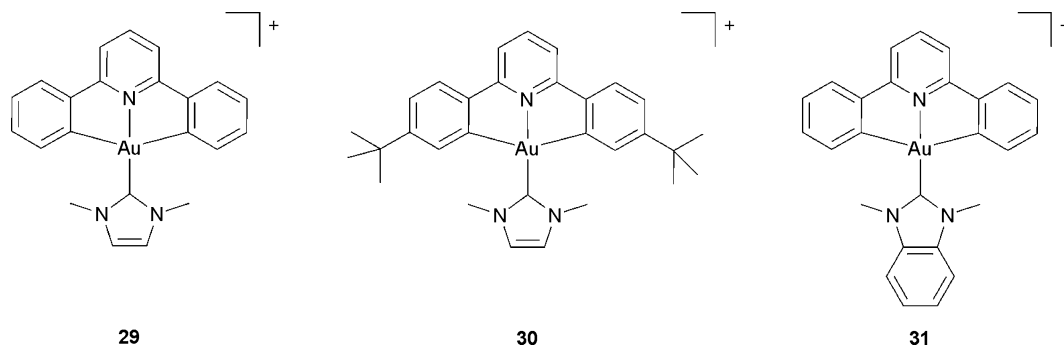
Scheme 8

long Au(III)–Au(III) distance in complex **28**, interpretation of the emission band shift in terms of an excimer character arising from intramolecular π–π interactions between C^N^C ligands was considered more plausible.[28] Indeed, an interplanar distance of 3.4 Å is close to ideal for π–π interactions. An analogous dimeric Au(III) complex with the longer 1,2-bis(diphenylphosphino)ethane (dppe) ligand (not shown) does not exhibit this phenomenon and emits at a similar wavelength as monomer **27**.[28]

Yam and co-workers recently reported on an entire series of organogold(III) complexes with tridentate C^N^C chelates and an *N*-heterocyclic carbene (NHC) ligand at the fourth coordination site of the Au(III) center.[31] In terms of electronic structure and metal coordination chemistry, NHCs are similar to tertiary phosphines (PR₃), yet, contrary to [Au(C^N^C)PPh₃]⁺ which is luminescent only at cryogenic temperatures, the NHC-complexes **29–31** (Scheme 9) are all emissive in fluid solution at room temperature.

The emission in these compounds is largely insensitive to the nature of the NHC ligand and contains a 1200–1300 cm⁻¹ vibrational progression. This, combined with the observation of large Stokes shifts and luminescence lifetimes in the microsecond regime, indicates that the emission originates from a metal-perturbed ³IL excited state. The [Au(C^N^C)Cl]⁺ parent complex is non-emissive under these conditions.[28] Thus it is clear that incorporation of the strongly σ-donating carbene ligands has a beneficial influence on the photoluminescence properties, most likely by raising the energy of d–d excited states. Aside from the mononuclear NHC-complexes **29–31**, several binuclear complexes were investigated and found to exhibit emission maxima at longer wavelengths (~10 nm) compared to the mononuclear congeners.[31] In the solid state, none of the Au(III)-NHC complexes investigated exhibited short Au(III)–Au(III) distances, but in several instances there are short separations (~3.4 Å) between C^N^C ligands that point to π–π stacking. This is the case for example in

binuclear complex **32** (Scheme 10), which exhibits two well-separated reduction waves in the cyclic voltamgramm, suggesting that there is significant electronic communication between its two square-planar coordination units. For complex **32**, the potential separation (ΔE) is 250 mV, for complex **33** with the longer alkyl-linker ΔE still amounts to 70 mV, while for complex **34** it became undetectably small. The observation of a potential separation for the (C^N^C ligand-based) reduction was attributed to a splitting of the π* LUMO on the C^N^C ligand into a lower lying and a higher lying dimer orbital caused by intramolecular π–π interactions between two cyclometalating ligands.

| **32** | n = 1 |
| **33** | n = 2 |
| **34** | n = 3 |
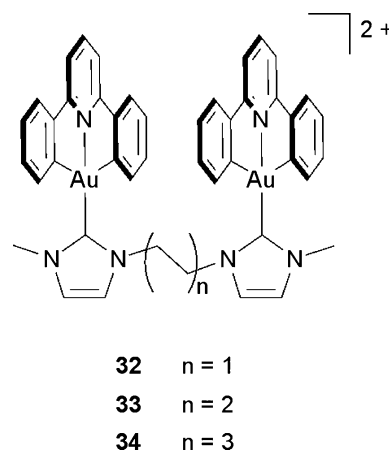
Scheme 10

Che and co-workers explored the potential of complex **32** and three other [Au(C^N^C)(NHC)] complexes as anticancer drugs.[32] Complex **32** binds to calf-thymus DNA with a binding constant of 5.4 × 10⁵ M⁻¹ at 298 K in Tris-buffered saline solution, whereupon its luminescence intensity increases by a factor of 5. In topoisomerase I, an enzyme that unwinds chromosomal DNA, complex **32** appeared to induce DNA strand breaks. Interestingly, the cytotoxicity of complex **32** appears to be more than 100 times higher for lung carcinoma cells than for ordinary (healthy) lung cells.

In 2005, Yam and co-workers noted that the chemistry of alkynylgold(III) complexes is essentially unexplored, and they gave a short report on luminescent [Au(C^N^C)(phenylacetylide)] complexes, which were the first of their kind.[33] As in their work on Au(III) complexes with NHC ligands discussed above, it was expected that introduction of strongly σ-donating ligands would

Scheme 9

35	R =	H
36	R =	Cl
37	R =	NO$_2$
38	R =	OCH$_3$
39	R =	NH$_2$
40	R =	N(C$_6$H$_5$)$_2$
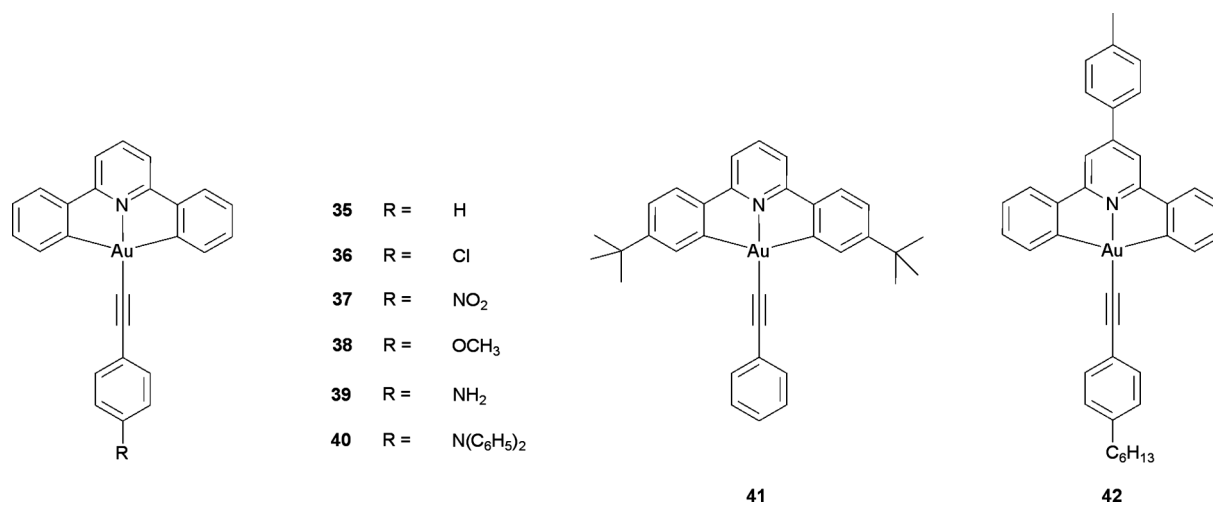
Scheme 11

lead to strong ligand fields and d–d excited states at very high energies. Indeed, this expectation was fulfilled for complexes **35**–**42** (Scheme 11), which are all emissive in solution at ambient temperature (Fig. 6).[33–35] These gold(III) diphenylpyridine complexes are structurally analogous to alkynylplatinum(II) complexes with terpyridine (N^N^N) or cyclometalating (C^N^N) ligands, which have been demonstrated previously to exhibit very rich photophysics and photochemistry.[36–38]
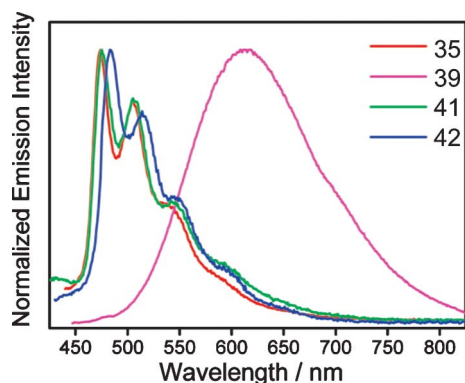
Fig. 6 Luminescence spectra of four [Au(C^N^C)(phenylacetylide)] complexes from scheme 11 in dichloromethane solution at 298 K. Adapted with permission from Ref. 35 Copyright 2007 American Chemical Society.

Complexes **35**–**38** exhibit virtually identical luminescence spectra in fluid dichloromethane with a maximum at 476 ± 2 nm and clear vibrational progressions corresponding to C≡C and C≡N stretching frequencies of the tridentate ligand (Fig. 6).[33,35] Thus, the emission of these compounds is assigned to IL luminescence of the cyclometalating chelate. Given the fact that the luminescence lifetimes are in the sub-microsecond to microsecond regime, the emissive state is likely to be of triplet parentage. Complex **39** is the only member in this family of complexes to exhibit markedly different emission properties: The luminescence spectrum of complex **39** in dichloromethane solution at 298 K is comprised of a broad and structureless band centered at 612 nm, *i.e.*, λ_{em} is red-shifted by roughly 4500 cm^{-1} compared to complexes **35**–

38. The amino-substituent renders the phenylacetylide ligand of complex **39** very electron-rich, hence it is plausible that emission of this complex originates from an excited state that is formed upon promotion of an electron from the aminophenylacetylide ligand to the 2,6-diphenylpyridine ligand, *i.e.*, an LLCT transition. This is similar to what has been found for complex **20** and several alkynylplatinum(II) complexes with amino-substituted phenylacetylide ligands.[39,40]

With respect to luminescence quantum yield (ϕ_{em}) and lifetime (τ_{em}), there are only minor differences between complexes **35**–**38** and complex **39**.[33,35] In fact, among these 5 complexes, ϕ_{em} varies only between 2 × 10^{-4} (**36**) and 2 × 10^{-3} (**39**), while τ_{em} is between 50 ns and 300 ns in dichloromethane at ambient temperature. At 77 K or in the solid state at 298 K, all 5 complexes exhibit broad and structureless emission bands. This is likely to be due to excimeric IL emission as a result of π–π interactions between stacked C^N^C ligands. Indeed, X-ray crystallographic studies of complexes **35**–**39** revealed interplanar separations between individual cyclometalating ligands ranging from 3.38 to 3.53 Å. However, most of the packing arrangements are such that head-to-tail arrangements of individual complexes are attained in the crystals, and as a consequence there are no short Au(III)–Au(III) contacts. Complex **38** exhibits the shortest intermolecular metal–metal contact, but the distance of 3.846 Å is still significantly larger than the sum of van-der-Waals radii of two gold(III) centers; hence there cannot be any significant metal–metal interaction.[41]

Electrochemical investigations by cyclic voltammetry show that the first reduction of these compounds involves the C^N^C ligand at potentials between −1.52 V and −1.59 V *vs.* SCE.[35] Only complex **37** with the nitro-substituted phenylacetylide ligand exhibits a reduction wave at more positive potential (−1.08 V *vs.* SCE), which has to be attributed to reduction of its electron-deficient phenylacetylide ligand. The electrochemical potentials for the first anodic waves are very sensitive to the nature of the alkynyl ligand and range from 0.76 V *vs.* SCE for complex **39** to 1.96 V *vs.* SCE for complex **37**. This, together with the fact that the Au(III) center is likely to be redox-inert, strongly suggests that the first oxidation of these complexes is associated with the phenylacetylide ligands. Unfortunately, no photoredox

properties have been reported yet. Given the fact that many [Pt(N^N^N)(alkynyl)]+ complexes exhibit rich photochemistry,[36,37] including for example the photosensitization of electron transfer reactions and the photochemical production of hydrogen,[38,42] this is definitely a subject that deserves further attention in future studies.

When the primary amino-group of complex 39 is replaced by a diphenylamino-substituent, the resulting complex (40) emits at an even longer wavelength (620 nm vs. 611 nm), because the LLCT transition is energetically lowered through increase of the electron density at the phenylacetylide ligand.[43] While the luminescence properties of most of the abovementioned complexes were only investigated after photoexcitation, complexes 35 and 40 were also investigated with respect to their electroluminescence properties.[43] Both compounds were successfully incorporated as dopants in OLEDs, and in the case of complex 40 it was even possible to tune the emission color through variation of the dopant concentration. A maximum external quantum efficiency of 5.5% and a luminance power efficiency of 14.5 lm W^{-1} are promising efficiency and brightness values for further investigations in the context of OLED applications.

Complex 40 was further explored with respect to electrogenerated chemiluminescence.[44] The principle of this excitation mode is to generate species at an electrode surface that then undergo electron transfer reactions to form emissive excited states. In the case of complex 40, a potential sweep over the range from –2 V vs. SCE to +2 V vs. SCE can create radical anions and radical cations of 40, which, in principle, can then react with each other to form one complex in its emissive excited state and another one in its ground state. However, because of the irreversibility of the oxidation process due to cation decomposition, this so-called "annihilation" luminescence cannot be observed for complex 40. However, when tri-n-propylamine (TprA) is used as a co-reactant, it is possible to observe electrogenerated chemiluminescence under carefully selected conditions. At an electrochemical potential of ca. 0.9 V vs. SCE, the TprA$^{·+}$ radical cation is formed. Subsequent loss of a proton by this organic cation forms a highly reducing radical species (TprA$^·$) that is thermodynamically capable of transferring an electron to complex 40, thereby forming 40$^-$. When this negatively charged complex reacts with a TprA$^{·+}$ cation, a sufficient amount of energy is liberated in order to form complex 40 in its excited state (>2.15 eV), as well as organic decomposition products associated with the TprA molecule. Consequently, electrogenerated chemiluminescence can be observed under these experimental conditions.

Complex 43 (Scheme 12) represents a further development of complex 40.[45] It not only has a strongly electron-donating phenylacetylide ligand such as complexes 39 and 40, but it has also an electron-withdrawing p-difluorophenyl unit attached to the C^N^C ligand. As a consequence, the LLCT emission maximum in complex 43 is further red-shifted to 669 nm (compared to 610 nm in 39 and 620 nm in 40). Its luminescence quantum yield (ϕ_{em}) is 8.5 × 10^{-3}, which is roughly a factor of 4 higher than that of complex 39.[45] Nanosecond transient absorption spectroscopy revealed a bleach between 300 and 350 nm that is attributed to depletion of the ground state and therefore weakened π–π* absorption of the C^N^C ligand in this wavelength range, while a positive signal around 520 nm was interpreted as a (4-diphenylaminophenyl)ethynyl radical cation absorption. This is

43
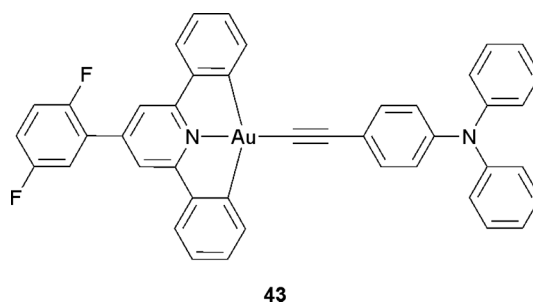
Scheme 12

indeed what would be expected for a LLCT state, but one would also expect to see evidence for the C^N^C radical anion between 380 and 420 nm. Unfortunately, this coincides with the spectral region of ground-state bleaching.

When doped into a poly(methyl methacrylate) (PMMA) matrix, the photoluminescence wavelength of complex 43 is strongly dependent on dopant concentration (Fig. 7), presumably due to the occurrence of excimeric emission at higher concentrations as a result of π-stacking of the C^N^C ligands. At any rate, the emission band maximum shifts from 538 nm at a dopant concentration of 2 wt.% to 575 nm at 50%. Likewise, the electroluminescence wavelength is strongly dependent on dopant concentration. At an optimized concentration of 4% in a 4,4′-N,N′-dicarbazole-biphenyl (CPB) layer of an OLED that is further comprised of an α-naphthylphenylbiphenyl diamine (NBP) hole-transporting layer and a tris(quinolinato)aluminium(III)-based electron-conducting layer, remarkably high efficiency and brightness were achievable. An external quantum efficiency of 11.5% and a power efficiency of 26.2 lm W^{-1} compare very favorably to OLED devices that are based on the widely used [Ir(2-phenylpyridine)$_3$] luminophor.[45]
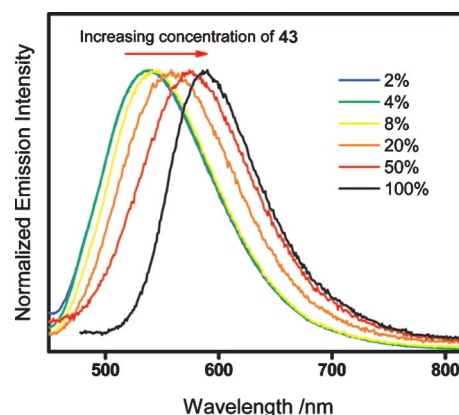

Fig. 7 Normalized photoluminescence spectra of complex 43 at different concentrations in thin films of PMMA at room temperature. Adapted with permission from Ref. 45 Copyright 2010 American Chemical Society.

The abovementioned experimental studies of [Au(C^N^C)-(alkynyl)] complexes did also stimulate in-depth computational work on such compounds. Recently, Zhang and co-workers reported on DFT studies of complex 35 and three related gold(III) complexes (44–46) (Scheme 13).[46] Of particular interest in these studies is the change of the electronic structure that results from variation of the tridentate ligand between C^N^C to

35

44

45

46

Scheme 13
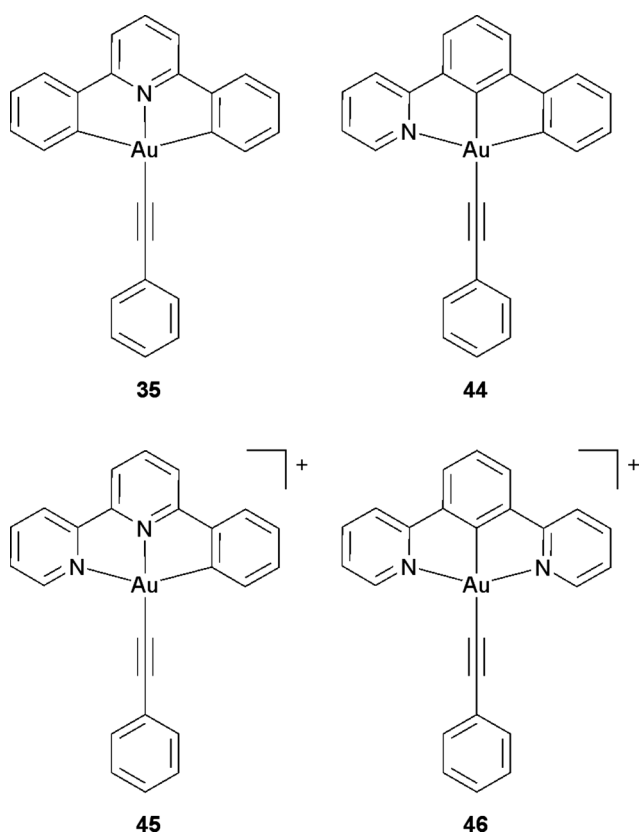
N^C^C, N^N^C, and N^C^N chelating modes. This is important computational work because there have been no experimental investigations of luminescent alkynylgold(III) complexes with the latter three ligand types so far – all of the abovementioned experimental studies involved exclusively C^N^C chelating ligands. Using a time-dependent DFT approach, the bond lengths between the metal center and the tridentate ligands were calculated to shorten upon excitation, while at the same time the bond lengths between Au(III) and the phenylacetylide ligand were calculated to elongate. This is in line with energetically low lying LLCT excitations involving electron promotion from the phenylacetylide to the cyclometalating ligand. For C^N^C complex **35**, this transition is calculated to occur at higher energy than in the three other complexes investigated, and the energetically lowest lying (and therefore emissive) excited state in this particular case appears to be a ^{3}IL state, which is in agreement with the experimental work by Yam and coworkers.[33–35] For N^C^C complex **44** and for N^N^C complex **45**, a ^{3}LLCT state appears to be the lowest electronically excited state, while for N^C^N complex **46** the lowest excited state is calculated to have mixed ^{3}LLCT/^{3}LMCT character.[46] The N^C^N system with a LUMO containing 41.5% metal character thus appears to be markedly different than the other three chelating modes, for which the contributions from Au atomic orbitals to the HOMO and LUMO orbitals is calculated to be less than 10%. Importantly, d–d excited states are consistently calculated to occur at high energies, and therefore all four types of alkynylgold(III) systems may potentially exhibit favorable emission properties. The stage is set for experimental investigations.

5. Synthetic challenges

Although the focus of this article is on the photophysical properties of cyclometalated gold(III) complexes, a few comments regarding challenges associated with the syntheses of the compounds from the previous sections seem to be in place. Direct cyclometalation of d^8 and d^6 metal ions requires rather drastic experimental conditions in many cases, typically refluxing in solvents with high boiling points for extended periods of time.[1,3,4] One of the difficulties that may be encountered with Au(III) is the formation of metallic gold,[27] but unfortunately this is by far not the only pitfall. There exists already a recent comprehensive review on the chemistry of gold(III) complexes with *bi*dentate C^N-donor ligands,[47] and it is therefore appropriate to focus here on even more recent work concerning the cyclometalation of Au(III) with *tri*dentate ligands. Stoccoro, Manassero and co-workers performed a systematic study of the reaction between H[AuCl$_4$]·3H$_2$O and 1,3-bis(2-pyridyl)benzene under various conditions and found that five different reaction products can be isolated (Scheme 14).[48]

Under very mild conditions (*i.e.*, in diethylether at room temperature), there is only the formation of the di-protonated salt (**47**). When carried out in refluxing acetonitrile for five days, the main reaction product is the mono-protonated salt (**48**). Dinuclear complex **49** is a minor by-product that is obtained in both cases, but it can be synthesized as a major product when putting salt **47** into reaction with one equivalent of NaHCO$_3$ in tetrahydrofuran.

The cyclometalated complex **50** is obtained when reacting H[AuCl$_4$]·3H$_2$O and 1,3-bis(2-pyridyl)benzene in acetic acid to which NaHCO$_3$ has been added, albeit only in a yield of ~40% even after seven days at reflux. Significant quantities of compounds **47** and **49** were identified as by-products, and a minor quantity of an additional compound, presumably complex **51**, is formed in the course of this reaction. An attractive alternative route to complex **50** involves the use of a transmetalation reaction that departs from the corresponding mercury(II) complex (**52**). This corresponds to a widely used method in the synthesis of late-transition metal pincer complexes.[47,49] Although the formation of the organomercury precursor (**52**) only occurs with a moderate yield of ~60%,[50] this is a useful procedure, because the subsequent transmetalation step affords complex **50** in ~90% yield.[48] In this case the [Au(N^C^N)Cl]$^+$ complex is obtained as a mercury salt, but the toxic anion can easily be exchanged by less toxic hexafluorophosphate.

An interesting case of metal-ion dependent regioselectivity was observed in the case of the 6-(2-thienyl)-2,2′-bipyridine ligand (**53**).[51] When stirring this ligand with K$_2$PtCl$_4$ in acetonitrile at room temperature, cyclometalation of platinum(II) readily occurs, and complex **54** can be isolated in nearly quantitative yield. By contrast, cyclometalation of gold(III) does not proceed as easily: With Na[AuCl$_4$], cyclometalation only occurs at reflux but the reaction product is not the expected complex in which ligand **53** covers three coordination sites of the metal center. Instead, a dinuclear complex (**55**) is formed in which only the terminal pyridine ring and the thiophene moiety of **53** are coordinated (Scheme 15).[51]

While coordination of the tridentate cyclometalating ligand is a crucial step, subsequent chemistry at the fourth coordination site of complexes such as **50** often proceeds much more smoothly. In some instances it is necessary to enforce displacement of the
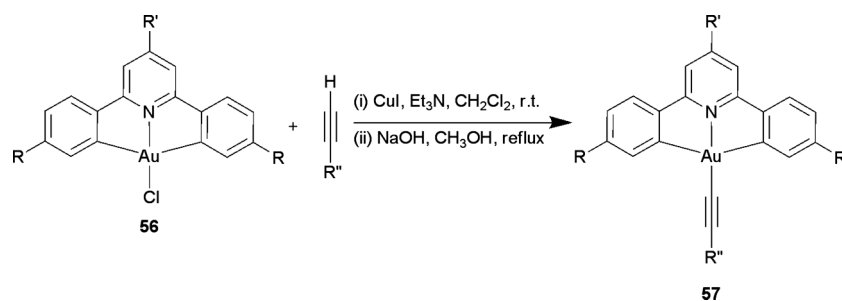
Scheme 14

Scheme 15
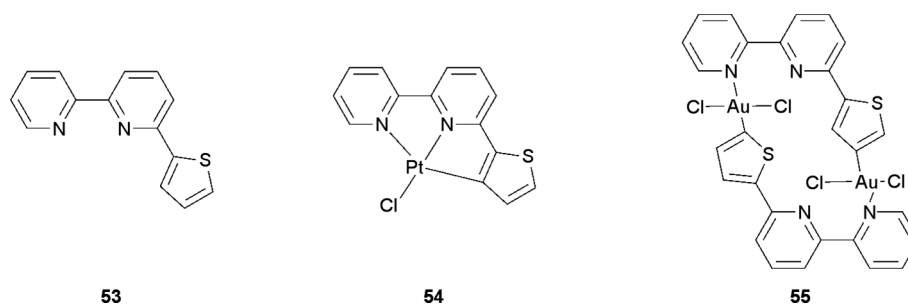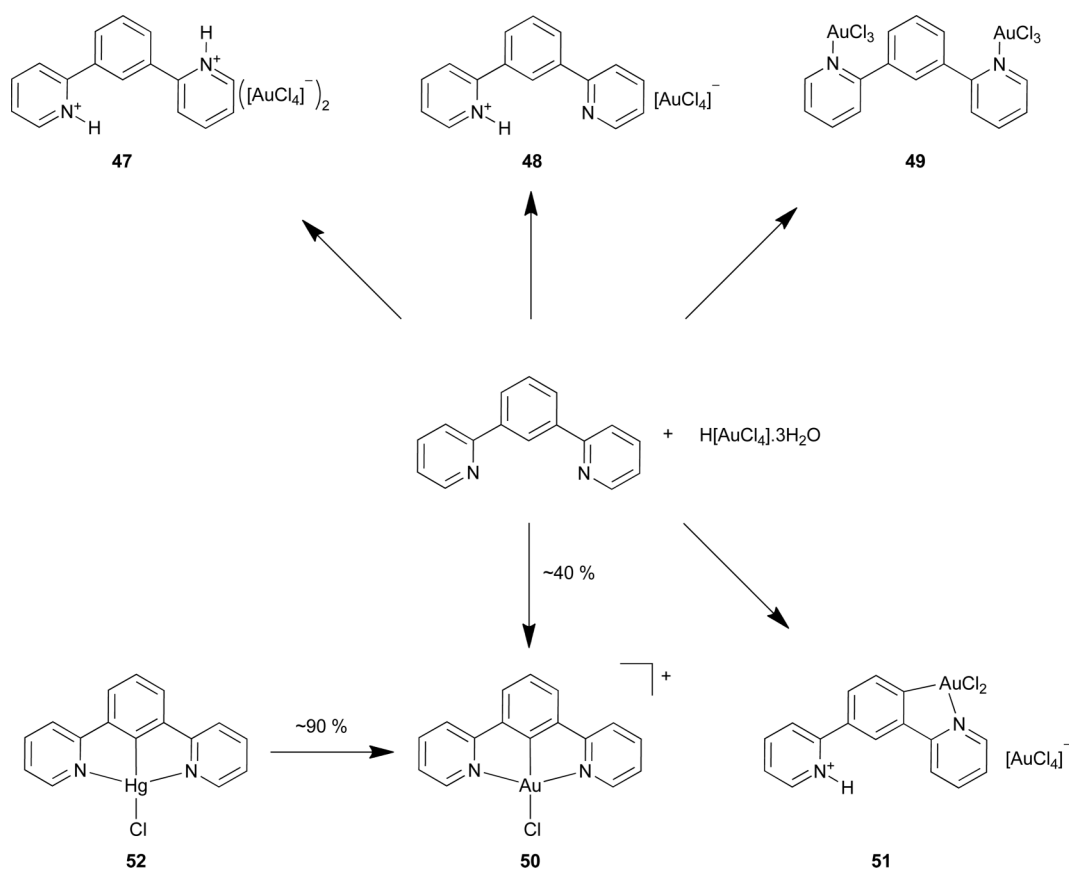
chloro-ligand through addition of silver(I) salts, but depending on the incoming ligand there exist a variety of different strategies for ligand substitution.[52] For obtaining luminescent cyclometalated gold(III) complexes, coordination of alkynyl ligands is particularly important. Yam and coworkers report that this is possible with two different methods (Scheme 16):[35] Method (i) employs a catalytic amount of CuI in a reaction mixture comprised of the chloro-gold(III) precursor, alkyne, and triethylamine in dichloromethane solvent. In the specific case of complexes **35–39**, stirring this mixture for 3 h at room temperature gives yields around 78 ± 10%. Method (ii) uses NaOH in methanol solvent, in which the chlorogold(III) precursor and the alkyne are refluxed for 12 h. This method gave yields around 40%.

Finally, we note that solubility appears to be an important issue for many of the luminescent cyclometalated gold(III) complexes

presented herein.[26] This is analogous to many square-planar complexes of platinum(II).[40]

6. Conclusions and outlook

While Au(I) is frequently stabilized by sulfur and phosphorous donor atoms, hard donors such as nitrogen, oxygen and carbon are useful to stabilize gold in its trivalent oxidation state. Cyclometalation with bi- and tri-dentate ligands is a viable strategy for obtaining luminescent gold(III) complexes, because the strongly σ-donating carbon ligand atom ensures strong ligand fields with high lying d–d excited states. Nonradiative relaxation from these states can thus be inhibited to a significant extent. However, for the ligand field to become sufficiently strong, usually more than one carbon donor atom is required. This is illustrated by

Scheme 16

the fact that the most efficient Au(III)-based emitters known to date are cyclometalated complexes with alkynyl or carbene ancillary ligands. The vast majority of these compounds exhibit intraligand phosphorescence (^{3}IL) in fluid solution, and hence the emission color appears to be tunable only to a somewhat limited extent, especially when compared to cyclometalated platinum(II) or iridium(III) complexes for which both ^{3}IL and ^{3}MLCT emission have been observed. On the other hand, research on luminescent cyclometalated gold(III) complexes is still much in its infancy, and there is yet much interesting photophysics and photochemistry to discover. For instance regarding tridentate cyclometalating ligands, research until now has focused almost exclusively on Au(III) complexes with C^N^C and C^N^N chelates, but there has been essentially no experimental work on N^C^N and N^C^C ligands. What is more, the photochemistry of cyclometalated gold(III) complexes is yet virtually unexplored. By analogy to isoelectronic alkynylplatinum(II) compounds, alkynylgold(III) complexes with long-lived excited states may potentially be useful for photochemical hydrogen production, or more generally speaking as photosensitizers for electron transfer reactions. An additional interesting aspect will be the exploration of metal–metal interactions in dimers and oligomers with short distances between individual cyclometalated Au(III) centers, and the investigation of the photophysical properties of such systems as a function of temperature and pressure.

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