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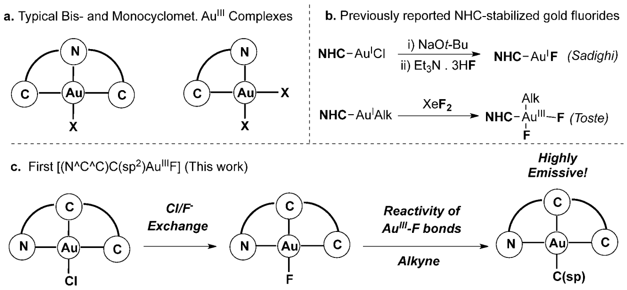
Luminescent (N^C^C) Gold(III) Complexes: Stabilized Gold(III) Fluorides

*Roopender Kumar, Anthony Linden, and Cristina Nevado**

Dedicated to Professor Antonio Echavarren on the occasion of his 60th birthday

Abstract: *We report the design, synthesis, and application of a (N^C^C)-ligand framework able to stabilize highly electron-deprived gold(III) species. This novel platform enabled the preparation of C(sp^2)-gold(III) fluorides for the first time in monomeric, easy-to-handle, bench-stable form by a Cl/F ligand-exchange reaction. Devoid of oxidative conditions or stoichiometric use of toxic Hg salts, this method was applied to the preparation of multiple [C(sp^2)-$\mathrm{Au^{III}}$-F] complexes, which were used as mechanistic probes for the study of the unique properties and intrinsic reactivity of Au–F bonds. The improved photophysical properties of [(N^C^C)$\mathrm{Au^{III}}$] complexes compared to classical pincer (C^N^C)-Au systems paves the way for the design of new late-transition-metal-based OLEDs.*



Scheme 1. a) Classical (C^N^C)-pincer and bidentate (N^C)-phenylpyridine gold(III) stabilized complexes (X = Halide, C(sp), C(sp^2)). b) Previously reported [(NHC)$\mathrm{Au^{I}}$F] and [(NHC)$\mathrm{Au^{III}AlkF_2}$] complexes. c) Novel [(N^C^C)$\mathrm{Au^{III}}$F] complexes by anionic ligand exchange reaction.

Gold(III) complexes have been underutilized compared to isoelectronic $\mathrm{Pt^{II}}$ and $\mathrm{Ir^{III}}$ species as additives to enhance the efficiency of organic light-emitting diodes (OLEDs).[1] The reason is two-fold: on the one hand, the $\mathrm{Au^{III}}$ center is highly electrophilic, and secondly, the presence of a low-energy d–d ligand field state that could quench the luminescence of the excited state by thermal equilibration or energy transfer represents an additional challenge. Among several others, pincer ligands based on dianionic 2,6-diphenylpyridine frameworks (C^N^C) have become excellent platforms for the stabilization of gold in high oxidation states as demonstrated by the seminal work of Che,[2] Yam,[3] and Bochmann.[4] Phenylpyridine (N^C)-$\mathrm{Au^{III}}$ species have also received increasing attention in this context (Scheme 1 a).[5] Promising emissive properties have been determined for many of these complexes.[2,3,4a,5b]

Transition metal fluorides reside at the heart of some of the most synthetically useful transformations in modern catalysis. While both, $\mathrm{Pd^{II}}$- and $\mathrm{Pd^{IV}}$-F complexes have been isolated and characterized as intermediates in fluorination and cross-coupling reactions,[6] reports on gold fluorides are, in contrast, extremely limited. In 2005, the first stabilized N-heterocyclic carbene [(NHC)$\mathrm{Au^{I}}$-F] complex was reported by Sadighi and co-workers (Scheme 1 b).[7,8] Recently, gold catalysts and electrophilic fluorinating agents have been effectively combined not only to produce new C–F bonds,[9a–c] but also C–C bonds through $\mathrm{Au^{I}}$/$\mathrm{Au^{III}}$ redox catalytic cycles.[9d–m] Although both, C(sp^2)- and C(sp^3)$\mathrm{Au^{III}}$F intermediates have been postulated, experimental evidence to substantiate the participation of these species in the above-mentioned transformations is to-date scarce. The major challenges include the need for strong oxidants to access gold in a high oxidation state, thus limiting the functional group compatibility, and the instability of the resulting oxidized metal complexes. Pioneering work from Toste and co-workers has shown that *cis*-[(NHC)$\mathrm{Au^{III}AlkylF_2}$] complexes, in equilibrium with the corresponding dimeric forms, can be obtained by oxidation of [(NHC)$\mathrm{Au^{I}}$Alkyl] with $\mathrm{XeF_2}$ (Scheme 1 b).[10] Interestingly though, a synthesis of gold(III) fluorides using classical pincer or phenylpyridine templates, devoid of oxidative conditions, is yet to be reported, likely owing to the insufficient stabilization of the electron deprived metal. We hypothesized that two consecutive C-anionic centers on the ancillary ligand could donate sufficient electron density to stabilize a highly electrophilic $\mathrm{Au^{III}}$ center. Thus, 3,5-disubstituted phenylpyridine ligands were designed with the aim of simultaneous double C(sp^2)-H functionalization of the aromatic rings (Scheme 1 c). We also envisioned that the central aromatic ring in such a N^C^C ligand would exert a strong *trans* influence that facilitates a direct anionic ligand exchange to produce the corresponding [$\mathrm{Au^{III}}$-F] complexes from the corresponding chlorides. Here, the first examples of monomeric, bench-stable [C(sp^2)$\mathrm{Au^{III}}$F] complexes are presented, and the unique properties and intrinsic reactivity of Au–F bonds have been studied. Notably, (N^C^C)$\mathrm{Au^{III}}$ species present enhanced emissive properties compared to the classical [(C^N^C)$\mathrm{Au^{III}}$] systems.

Ligands **La–j** (Table 1) were prepared by Suzuki–Miyaura cross-coupling between commercially available 2-bromo-3-

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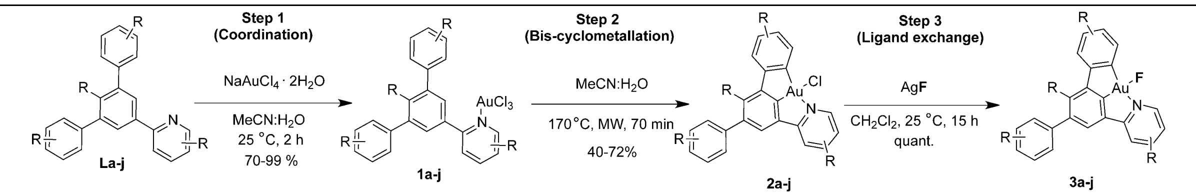
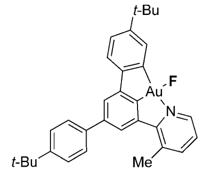
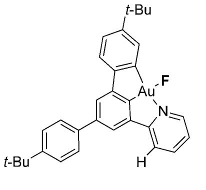
Table 1: Synthesis of [(N^C^C)Au^{III}F] complexes.

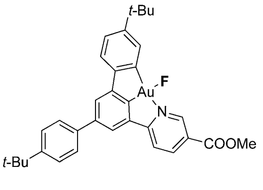




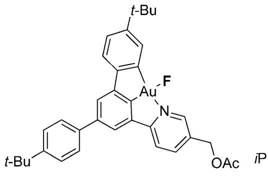
Step 1: **1a**, 99% (X-Ray)
Step 2: **2a**, 72% (X-Ray)
Step 3: **3a**, quant.



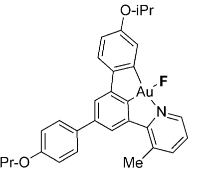
Step 1: **1b**, 98%
Step 2: **2b**, 57%
Step 3: **3b**, quant.



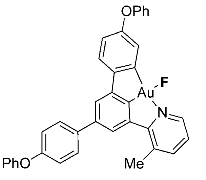
Step 1: **1c**, 70%
Step 2: **2c**, 44%
Step 3: **3c**, quant.



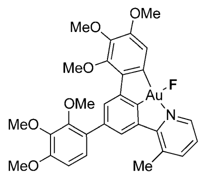
Step 1: **1d**, 80%
Step 2: **2d**, 51% (X-Ray)
Step 3: **3d**, quant. (X-Ray)



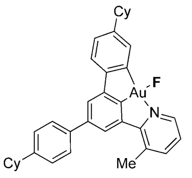
Step 1: **1e**, 95%
Step 2: **2e**, 63%
Step 3: **3e**, quant.



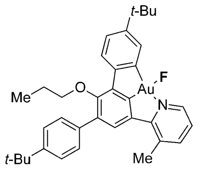
Step 1: **1f**, 97%
Step 2: **2f**, 59%
Step 3: **3f**, quant.



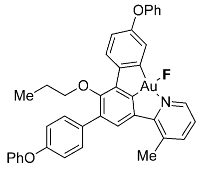
Step 1: **1g**, 92%
Step 2: **2g**, 55%
Step 3: **3g**, quant.



Step 1: **1h**, 96%
Step 2: **2h**, 47%
Step 3: **3h**, quant.



Step 1: **1i**, 94%
Step 2: **2i**, 40%
Step 3: **3i**, quant.



Step 1: **1j**, 98%
Step 2: **2j**, 40%
Step 3: **3j**, quant.

substituted pyridines and 3,5-bisaryl-substituted phenyl boronic acids.[11] Treatment of **La–j** with [NaAuCl$_4$]·2H$_2$O in an acetonitrile/water mixture at 25 °C for 2 h resulted in the formation of **La–j**AuCl$_3$ complexes **1a–j** in 70–99 % yields. X-ray diffraction analysis of compound **1a** validated the proposed structure (Figure 1).[11] Next, the reactions of complexes **1** in acetonitrile/water 1:1 at 170 °C in the microwave for 70 min delivered bis-cyclometalated products **2** in 40–72 % yields.[12]

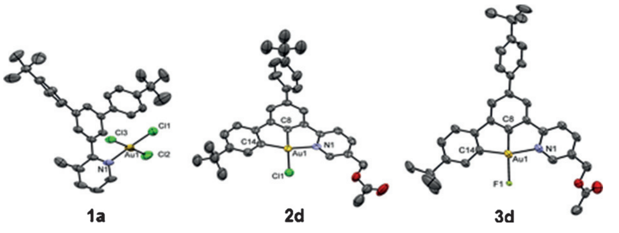
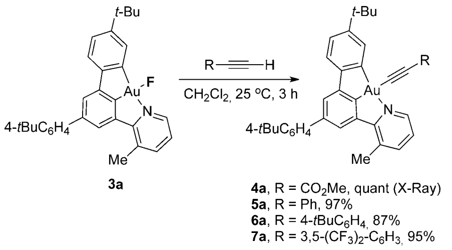


Figure 1. The solid-state molecular structures of **1a**, **2d**, and **3d** are shown with atoms drawn using 50 % probability ellipsoids. The *trans* influence of the central C(sp^2)-atom of the ligand results in an elongated Au(1)-X(1) bond.[2c,10a] **2d**: Au(1)-Cl(1) = 2.3602(19) Å. **3d**: Au(1)-F(1) = 2.264(3) Å. A distorted square planar geometry was confirmed with the trans angles around the Au^{III} center deviating significantly from ideal values. **2d**: N(1)-Au(1)-C(14) = 160.5(3). **3d**: N(1)-Au(1)-C(14) = 160.3(3).

Substituents on the pyridine ring were well tolerated although slightly lower yields were observed for electron-withdrawing groups (**2a–d**). The substitution pattern on the 3,5-aryl moieties was also studied: 4-isopropoxy- (**1e**), 4-phenoxy- (**1f**), 2,3,4-trimethoxy- (**1g**) and 4-cyclohexyl- (**1h**) substituted bis-cycloaurated adducts **2e–h** could be prepared in good yields. Substitution on the central phenyl ring could also be accommodated, as shown in compounds **2i** and **2j**. Single crystals of complexes **2a** and **2d** confirmed the structural assignments (Figure 1).[11] This two-step procedure to access chlorides **2** avoids the use of mercury compounds, which are employed as precursors for the synthesis of classical pincer [(C^N^C)Au^{III}Cl] complexes, by transmetalation between the mercury species and [HAuCl$_4$].[2–4,13]

Exchange of the chloride ligand to produce the desired [(N^C^C)Au^{III}F] (**3**) was carried out by treatment with silver fluoride in dry CH$_2$Cl$_2$ at room temperature, providing full conversion of the starting materials after 12 h. The reactions were monitored by both ^{1}H and ^{19}F NMR, which indicated the clean formation of the Au−F bond with a characteristic ^{19}F NMR resonance in the δ −(230–225) ppm range (C$_6$D$_6$). Complexes **3** were insensitive towards light, air, or even water and proved to be stable in its monomeric form for weeks at room temperature in the solid state as well as in solution in chlorinated solvents. Suitable, albeit disordered, crystals of compound **3d** could be obtained by slow diffusion of hexane into a concentrated solution of the complex in dichloromethane, enabling the confirmation of both composition and structure (Figure 1).[11] These results confirmed that the N^C^C framework can overcome the weak *trans* ligand-directing effect[14] of the pyridine moiety in classical C^N^C systems in which a direct ligand exchange reaction on the gold(III)-chloride bond, even in the presence of silver salts, is sometimes difficult to attain.[4a]

The reaction of complex **3a** with terminal alkynes was investigated. Treatment with methyl propiolate in dichloromethane at 25 °C for 3 h yielded, after evaporation of the solvent, [Au^{III}akynyl] complex **4a**, whose structure was confirmed by X-ray diffraction analysis.[11] Phenyl acetylene produced the corresponding alkynyl complex **5a** in almost quantitative yield. Other aryl substituted alkynes reacted in an analogous manner so that [(N^C^C)Au^{III}Alkynyl] complexes **6**–**7a** could be obtained in high yields (Scheme 2). The intrinsic lability of the Au–F bond can be compared to that of previously reported weakly bound Au–alkoxide ligands.[4a]



Scheme 2. Synthesis of [(N^C^C)Au^{III}Alkynyl] complexes **4**–**7a**.

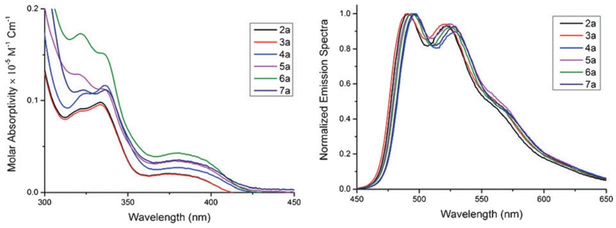


Figure 2. Photophysical data for complexes **2**–**7a**. Top left: UV/Vis absorption spectra in dichloromethane. Top right: Emission spectra measured in degassed CH_2Cl_2 (10^{-5} M) at room temperature.

We recognized that the N^C^C ligand framework could not only render the Au^{III} more electron-rich, but also raise the energy of the d–d states and thereby increase the chances of populating emissive states, in turn fostering luminescence properties as predicted by DFT calculations.[15] For this reason, the photophysical properties of **2--7a** were also studied (Figure 2, Table 2). These complexes showed intense absorption bands at 320–337 nm and a broad vibronic-structured, moderately intense absorption band at 375–381 nm with extinction coefficients ε in the order of $>10^3\,\text{M}^{-1}\,\text{cm}^{-1}$ in dichloromethane solution at 25 °C. Given the similar absorption bands detected for all complexes despite the different non-ancillary anionic ligand (Cl-, F-, and acetylides), the possibility of ligand-to-metal or ligand-to-ligand charge transfer transitions (LMCT and LLCT, respectively) can be excluded. Hence, the characteristic absorption bands can be assigned to metal-perturbed intraligand (IL) transitions localized on the N^C^C ligand. As no Au$^{III}\cdots$Au^{III} interaction was observed in any of the crystal structure analyses,[11] the presence of metal-to-metal-to-ligand charge transfer (MMLCT) transitions can also be discarded.

Table 2: Photophysical properties for complexes **2**–**7a**

Cmp.	Absorption λ_{max} [nm] (ε_{max} [$M^{-1}\,cm^{-1}$])	Emisssion λ_{max} [nm] (τ_0 [μs])[a]	ϕ_{em} [b]	k_r $\times 10^3$ [s^{-1}][c]	k_{nr} $\times 10^4$ [s^{-1}][d]
2a	322(9093), 334-(9797), 375(2039)	491, 522 (56)	0.17	3.0	1.4
3a	322(8857), 334-(9542), 375(1986)	489, 522 (55)	0.27	4.9	1.3
4a	325(10781), 336-(11644), 381-(2705)	497, 528 (54)	0.16	2.9	1.5
5a	320(12880), 334-(11282), 378-(3478)	494, 526 (63)	0.27	4.2	1.1
6a	323 (11158), 337-(11165), 381-(3531)	496, 527 (80)	0.16	2.0	1.0
7a	322(17268), 335-(15157), 381-(4248)	494, 526 (60)	0.28	4.6	1.2

[a] Phosphorescence lifetime. [b] Phosphorescence quantum yield measured at 1×10^{-5} mol dm^{-3} at room temperature. [c] Radiative decay rate constant estimated by $k_r = \varphi/\tau$. [d] Non-radiative decay rate constant estimated by $k_{nr} = (1-\phi)/\tau$.

Interestingly, complexes **2**–**7a** showed a strong luminescence upon excitation at $\lambda \geq 335$ nm in degassed dichloromethane at room temperature. All of these compounds exhibit almost similar intense vibronic-structured emission bands with peak maxima at 489–497 nm. These emissions are assigned to a metal-perturbed ^{3}IL (π-π*) transition of the N^C^C ligand. Their solution emission quantum yields are in most cases over 0.16 and up to 0.28, a remarkable value in the arena of gold(III) emissive compounds. Besides the commonly encountered acetylides or NHC sigma donor ligands, also chloride and even a fluoride ligand are able to activate the intraligand state (^{3}IL) emission of the corresponding cyclometalated Au^{III} complexes, with 0.17 and 0.27 quantum yields, respectively. As such, the remarkable luminescent behavior of these compounds needs to stem from the special arrangement of the N^C^C scaffold.[16] Unlike most Au^{III} compounds, which exhibit luminescence only at low temperature or are non-emissive, complexes **2**–**7a** display luminescence in solution at ambient temperature and are comparable or even improve the performance of emissive classical (C^N^C)-pincer and (N^C)-phenylpyridine Au^{III} complexes.[2,3,4a,5b,17]

In summary, a novel N^C^C pincer framework, able to stabilize gold in high oxidation state, is reported here. The first examples of C(sp^2)-gold(III) fluorides obtained through a mild Cl/F ligand exchange reaction have been described. These new Au^{III}F species are stabilized through a carefully designed ligand system that balances the electronic needs of the metal, yielding monomeric, bench-stable, complexes. Discrete [(N^C^C)Au^{III}F] species were used as chemical probes to gain a deeper understanding of elementary reactivity of Au–F bonds. The improved photophysical properties measured for the [(N^C^C)Au^{III}] complexes represent a valuable addition to the current portfolio of classical pincer (C^N^C)- and (N^C)-$\mathrm{Au^{III}}$ emissive species.

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Keywords: anionic ligand exchange · fluoride · gold · organic light-emitting diodes · pincer complexes

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[11] For further details, please, see the Supporting Information. X-Ray diffraction analysis data are available from the CCDC database: CCDC 1033830 (**1a**), 1033772 (**2a**), 1058552 (**2d**), 1033763 (**3d**) and 1033775 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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