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Synthesis of New Donor-Substituted Biphenyls: Pre-ligands for Highly Luminescent (C[^]C[^]D) Gold(III) Pincer Complexes

Wolfram Feuerstein,^[a] Christof Holzer,^[b] Xin Gui,^[c] Lilly Neumeier,^[a] Wim Klopper*^[d] and Frank Breher*^[a]

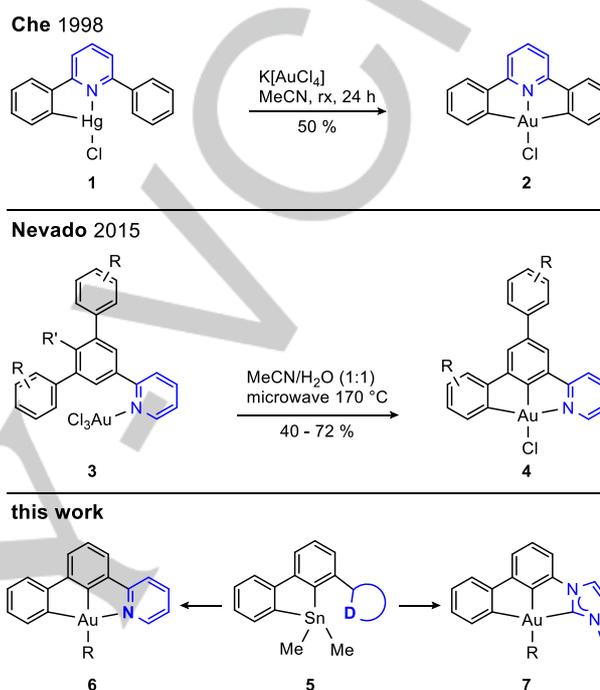
Abstract: We herein report on new synthetic strategies for the preparation of pyridine and imidazole substituted 2,2'-dihalo biphenyls. These structures are pre-ligands suitable for the preparation of respective stannoles. The latter can successfully be transmetalated to K[AuCl₄] forming non-palindromic [(C[^]C[^]D)Au^{III}] pincer complexes featuring a lateral pyridine (D = N) or *N*-heterocyclic carbene (NHC, D = C') donor. The latter is the first report on a pincer complex with two formally anionic sp² and one carbenic carbon donor. The [(C[^]C[^]D)Au^{III}] complexes show intense phosphorescence in solution at room temperature. We discuss the developed multi-step strategy and touch upon synthetic challenges. The prepared complexes have been fully characterized including X-ray diffraction analysis. The gold(III) complexes' photophysical properties have been investigated by absorption and emission spectroscopy as well as quantum chemical calculations on the quasi-relativistic two-component TD-DFT and GW/Bethe-Salpeter level including spin-orbit coupling. Thus, we shed light on the electronic influence of the non-palindromic pincer ligand and reveal non-radiative relaxation pathways of the different ligands employed.

Introduction

Phosphorescent emitters based on gold(III)^[1] are far less studied in the context of phosphorescent organic light-emitting diodes (PhOLEDs)^[2] than systems incorporating other heavy metals, e.g. iridium(III),^[3] ruthenium(II)^[4] or platinum(II).^[5] However, there is increasing interest in gold(III)-based systems mainly employing a 2,6-diphenylpyridine (C[^]N[^]C)-based pincer ligand.^[6] The (C[^]N[^]C) pincer diminishes radiationless relaxation pathways of excited complexes due to its rigid nature^[7] and – in combination with an additional strong donor ligand – results in high ligand field splitting thereby shifting metal-centred d-states to higher energies. The latter avoids population of these metal centred states regularly seen to be responsible for radiationless relaxation pathways.^[8]

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Scheme 1. Preparation of palindromic (C[^]N[^]C) and non-palindromic (C[^]C[^]N) Au^{III} complexes reported in the literature and the synthetic approach presented in this study. D: Donor.

The first example of [(C[^]N[^]C)Au^{III}] complexes luminescent in frozen solution at 77 K was reported by Chi-Min Che and co-workers in 1998.^[9] In 2005, Vivian Wing-Wah Yam and co-workers combined the (C[^]N[^]C) motif with alkynyl ligands to obtain Au^{III} complexes which show phosphorescence in solution at room temperature.^[10] Later on, the field of luminescent [(C[^]N[^]C)Au^{III}] complexes was further broadened by employing carbenes,^[11] alkyl donors^[12] or thiolates^[13] as ancillary ligands. The pincer's structure was modified as well, e.g. by substituting the central pyridine by pyrazine, thus, affecting emission quantum yields and wavelengths.^[14]

We note that highly emissive tetradentate Au^{III} complexes reported only recently may outperform many tridentate systems in this regard,^[15] however, complexes with tetradentate ligands are less attractive for possible applications in chemical or catalytic transformations because all coordination sites of the central Au^{III} atom are occupied. That [(C[^]N[^]C)Au^{III}] complexes are valuable candidates for the latter applications could impressively be shown by Bochmann and co-workers who reported on the synthetic value of [(C[^]N[^]C)Au^{III}] hydroxides^[16] and hydrides.^[17] In addition, they prepared [(C[^]N[^]C)Au^{III}] olefin^[18] and alkyne complexes^[19] thereby showing the suitability of these complexes for C–C bond forming reactions. Finally, some [(C[^]N[^]C)Au^{III}] complexes are investigated in the realm of anticancer drug research^[20] with a

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very recent study about photo-activatable cytotoxic [(C^{^A}N^{^C})Au^{III}] hydrides.^[21]

The (C^{^A}N^{^C}) motif is introduced by reacting a mono-cyclometalated mercury compound like **1** with gold(III) salts (Scheme 1). In 2015, Nevado and co-workers reported on the synthesis of the non-palindromic^[22] [(C^{^A}C^{^A}N)Au^{III}] analogue which exhibits exchanged positions of the central pyridine ring and one lateral phenyl donor (**4** in Scheme 1).^[23] The latter is prepared without need for toxic mercury compounds in an elegant way by means of two successive, microwave-assisted C–H activations, using pyridine substituted terphenyls designed to allow only one kind of twofold cyclometalated products.

The non-palindromic (C^{^A}C^{^A}N) pincer was shown to exhibit high emission quantum yields making its gold(III) complexes particularly interesting for OLED fabrication.^[24] This was assigned to a higher ligand field splitting of these complexes compared to the palindromic (C^{^A}N^{^C}) congeners which was investigated by TDDFT.^[8b, 25]

The central phenyl donor of the (C^{^A}C^{^A}N) ligand exhibits a stronger *trans* influence than the (C^{^A}N^{^C})'s central pyridine. This made the preparation of stable Au^{III} fluorides^[23] and formates^[26] possible and finds expression in notably different NMR shifts of the respective hydrides.^[17b] Moreover, the *trans* influence affects the complexes' reactivity: [(C^{^A}C^{^A}N)Au^{III}] carboxylates favour thermal decarbonylation reactions^[27] whereas the (C^{^A}N^{^C}) based carboxylates show elimination of CO₂.^[28]

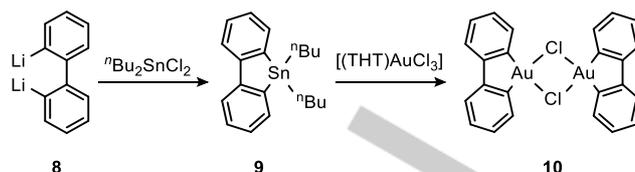
There are no reports in the literature on gold(III) pincer complexes with two aryl donors and a third donor other than pyridine (D = N), e.g. carbene. However, bidentate, (C^{^A}C^{^C}) cyclometalated (C^{^C} = NHC carbon donor) Au^{III} complexes were reported by von Arx *et al.*^[29] and Crespo *et al.*^[30]

In the present study, we report on the development of a synthetic access to 5,5-dimethyl-5*H*-dibenzo[*b,d*]stannoles (**5**) with a pyridine (D = N) or imidazolium (D = C⁺) substituent in 4-position, which are suitable precursors for the new Au^{III} complexes **6** and **7** (Scheme 1). On the one hand, this synthetic approach constitutes a complementary variant of the synthesis developed by Nevado and co-workers to prepare non-palindromic [(C^{^A}C^{^A}N)Au^{III}] complexes. On the other hand, it is the first example of a transition metal pincer complex with one NHC and two formally anionic phenyl donors. Both pincer complexes are combined with phenylethynyl or pentafluorophenyl ligands resulting in compounds highly phosphorescent in solution at room temperature. The photophysical properties are investigated experimentally and by means of TDDFT and the Bethe-Salpeter methodology including spin-orbit coupling described by us only recently,^[31] thereby showing the utility of these methods in the field of photophysics and photochemistry.

Results and Discussion

Retrosynthetic Considerations

Our synthetic approach for the preparation of non-palindromic [(C^{^A}C^{^A}D)Au^{III}] complexes (D = pyridine, NHC) is based on the synthesis of biphenyldiyl gold(III) dimer **10** by transmetalation of the stannole **9** with gold(III) salts, already described by Usón *et al.* in 1980 (Scheme 2).^[32]

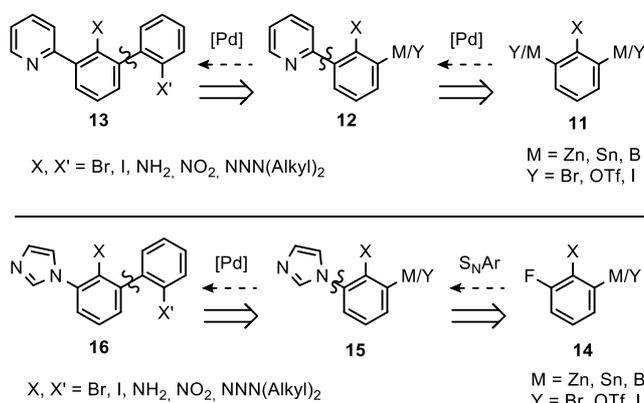


Scheme 2. Preparation of biphenyldiyl gold(III) dimer **10** according to Usón *et al.*^[32]

Direct transmetalation of dilithiobiphenyls to Au^{III} is only possible for very electron-poor biphenyls like perfluorinated ones^[33] or special Au^{III} precursors^[34] due to the tendency of Au^{III} to become reduced by organometallic reagents. Besides the findings of Toste,^[35] Bourissou^[36] and Bertrand^[37] on the oxidative addition of biphenylene to several Au(I) species, the transmetalation of stannoles is the method of choice for the preparation of cyclometalated biphenyldiyl Au^{III} complexes.^[34, 38] Thus, we anticipated the corresponding 4-substituted stannoles **5** would be equally useful for the preparation of non-palindromic (C^{^A}C^{^A}D) complexes of gold.

Dilithiobiphenyl **8** may be prepared by reaction of biphenyl with two equivalents of ⁿBuLi,^[39] however, this variant suffers from low yields and regioselectivity when employing substituted biphenyls. Therefore, we focused on the synthesis of 2,2'-dihalobiphenyls **13** and **16** with bromo or iodo substituents (Scheme 3), which should serve as suitable pre-ligands for the preparation of the pursued stannoles **5** (Scheme 1).

The anticipated dihalobiphenyls **13** and **16** should be accessible by introducing a 2-halophenyl to phenylpyridine **12** and phenyl imidazole **15** by means of palladium catalysed C–C cross-couplings. The halogens may be obtained by transformation of suitable N-based functional groups, i.e. anilines (X, X' = NH₂), nitrobenzenes (X, X' = NO₂) or triazenes (X, X' = NNNR₂), by means of SANDMEYER type reactions,^[40] eventually after reduction of NO₂. The latter must be performed after building the core pincer structure to ensure selectivity of the C–C cross couplings. Phenylpyridine **12** might be obtained by C–C cross coupling as well starting with **11** having (pseudo)halogen or metal substituents in 2- and 6-position. Imidazole (**15**) should be introducible by means of nucleophilic aromatic substitution at 2-fluoro nitrobenzene **14**.

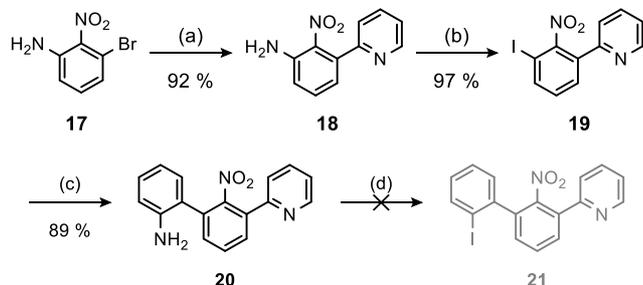


Scheme 3. Retrosynthetic aspects of the preparation of dihalobiphenyls with pyridine (C^{^A}C^{^A}N) (**13**) or NHC (C^{^A}C^{^A}C⁺) (**16**) donor. [Pd]: Pd catalysed C–C cross coupling.

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Pre-Ligand Synthesis

With the above mentioned strategy at hand, we first coupled commercially available nitroaniline **17** with 2-(tributylstannyl)pyridine^[41] followed by diazotization-iodination to obtain iodine substituted phenylpyridine **19** in excellent yield.

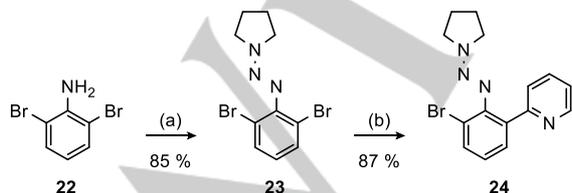


Scheme 4. Attempt to obtain biphenyl **21**. Conditions: (a) 2-(tributylstannyl)pyridine, LiCl, [Pd(PPh₃)₄] (4 mol%), xylene, rx, 6 h; (b) 1) HCl, NaNO₂, H₂O, 0 °C, 30 min 2) KI, 0 °C → rt, 12 h; (c) 2-(aminophenyl)boronic acid, K₃PO₄, XPhos Pd G₃ (3 mol%),^[42] 1,4-dioxane/H₂O (4:1), 70 °C, 90 min; (d) 1) HCl, NaNO₂, H₂O, 0 °C, 30 min 2) KI, 0 °C → rt, 12 h. The structure of **20** in the solid state could be determined by X-ray diffraction analysis (Figure S 9, SI).

Iodide **19** was then coupled with 2-(aminophenyl)boronic acid by means of a SUZUKI-MIYAJI coupling.^[42-43] Unfortunately, diazotization-iodination of **20** failed, although there are reports on the successful diazotization-iodination of 2'-nitro-2-phenyl-anilines.^[44]

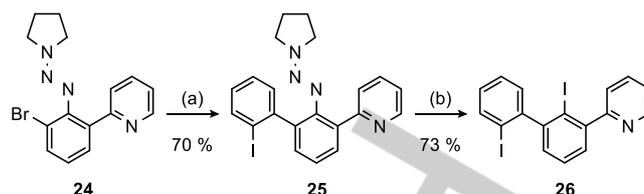
Beside the classical variant using HCl/NaNO₂/KI, we also tried DMSO-based reagents^[45] or modifications employing CuBr₂.^[46] Substitution of NH₂ by Me₃Sn according to a diazotization-stannylation protocol led only to unidentified decomposition products.^[47] Attempts to isolate the corresponding diazonium salt employing H[BF₄]/NaNO₂ or [NO][PF₆] were unsuccessful as well. Reduction of the nitro-group of **20** and subsequent double diazotization-iodination of the resulting amines is not effective, because 2,2'-diaminobiphenyls cyclize to the corresponding benzo[c]cinnolines under diazotization conditions.^[48] We also directly introduced 2-bromophenyl to **19**, however, this approach lacked of unacceptably low yields (Section S 1.2, SI).

We then turned our attention to a different approach based on the triazene **23** as key structure which was described by Knochel and co-workers in the context of carbazole syntheses.^[49] Magnesium using *turbo*-Grignard,^[50] subsequent transmetalation with ZnBr₂ and reaction with 2-bromopyridine by means of a NEGISHI-coupling^[40, 51] gave **24** in 87% isolated yield.



Scheme 5: Synthesis of triazene **24**. Conditions: (a) 1) HCl, NaNO₂, H₂O, 0 °C, 30 min 2) K₂CO₃, pyrrolidine, MeCN, 0 °C → rt, 2 h; (b) 1) ^tPrMgCl·LiCl, THF, -40 °C → -15 °C, 4 h 2) ZnBr₂, -20 °C → 5 °C, 1 h 3) 2-bromopyridine, [Pd(PPh₃)₄] (10 mol%), reflux, 16 h.

Then, we prepared the corresponding NEGISHI-reagent of **24** and coupled with 1,2-diiodobenzene to yield **25** (Scheme 6).

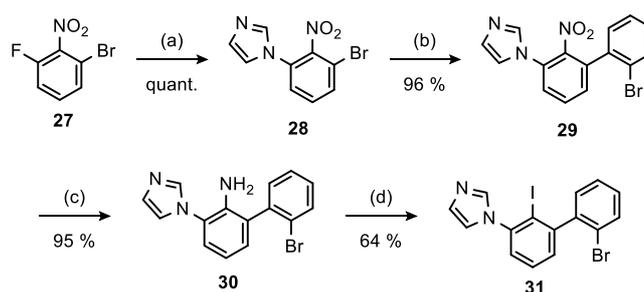


Scheme 6: Synthesis of diiodo biphenyl **26**. Conditions: (a) 1) ^tBuLi (pre-cooled to -78 °C), -100 °C, 90 min 2) 1M ZnBr₂ in THF (pre-cooled to -78 °C), -100 °C → -78 °C, 1 h, rt, 1 h 3) 1,2-diiodobenzene, [Pd(PPh₃)₄] (5 mol%), rx, 16 h; (b) Amberlyst 15[®], KI, MeCN, 70 °C, 10 min. The structure of **25** in the solid state could be determined by X-ray diffraction analysis (Figure S 9, SI).

The latter was only successful under meticulous temperature control: **24** was lithiated at -98 °C with precooled (-78 °C) ^tBuLi in hexanes and subsequently transmetalated with ZnBr₂ to obtain a NEGISHI-reagent suitable for coupling with 1,2-diiodobenzene. Prior to that, we tried magnesiation of **24** using *turbo*-Grignard which did not occur even at elevated temperatures (THF, 80 °C) leaving the bromide unaffected. The same holds for attempts to directly zincate **24** using elementary zinc prepared by the method of Rieck^[52] or in the presence of LiCl.^[53] This is probably rooted in the electron-rich nature of **24** in contrast to the substrates reported by the group of Knochel^[53a] who used only electron-deficient triazenes for direct zinc insertions. Reacting **24** with elementary magnesium led only to decomposition products even in the presence of ZnCl₂. Consequently, we tried to lithiate **24** and transmetalate with ZnBr₂. Under standard conditions (^tBuLi or two eq. ^tBuLi -78 °C) we detected only decomposition products, maybe due to decomposition by α -deprotonation at the pyrrolidine which is known to readily happen at higher temperatures.^[54]

The triazene **25** decomposes in the presence of HI^[55] to the diiodo biphenyl **26**. We identified a variation employing proton exchange resin and sodium iodide, i.e. *in situ* formed HI, in dry acetonitrile to be the most effective.^[56] This procedure avoids shortcomings of other variations, e.g. reactions at the pyridine ring.^[57]

For the preparation of a (C[∧]C[∧]C[∧]) pre-ligand we started with commercially available 1-bromo-3-fluoro-2-nitrobenzene (**27**) (Scheme 7).



Scheme 7. Synthesis of (C[∧]C[∧]C[∧]) pre-ligand **31**. Conditions: (a) Imidazole, NaOH, DMSO, rt, 2 h; (b) 2-bromophenyl boronic acid, [Pd(PPh₃)₄] (5 mol%), K₂CO₃, THF/H₂O (2:1), rx, 18 h; (c) Fe, EtOH/HOAc (1:1), rx, 3 h; (d) 1) 6 M HCl, NaNO₂, 0 °C, 30 min 2) KI, 0 °C → rt, 3 h. The structure of **29** in the solid state could be determined by X-ray diffraction analysis (Figure S 9, SI).

After introduction of imidazole by means of a nucleophilic aromatic substitution^[58] (**28**), we introduced 2-bromophenyl (**29**) and subsequently reduced the nitro group to obtain the aniline **30**. The latter tends to cyclize with triazine formation (Section S 2.1, SI), however, under strongly acidic conditions the dihalobiphenyl **31** can be obtained in 64 % yield, corresponding to a good overall

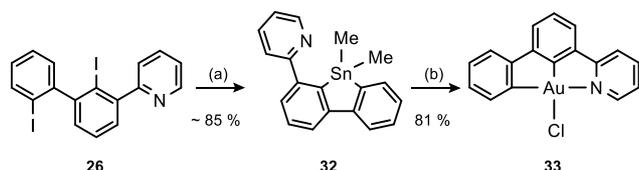
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yield of 58 % over four steps. The presented route is especially attractive, since all intermediates may be used without purification.

Although several synthetic steps are necessary, the dihalobiphenyls **26** and **31** are easily preparable on a 10 to 20 g scale.

Complex Synthesis and Characterization

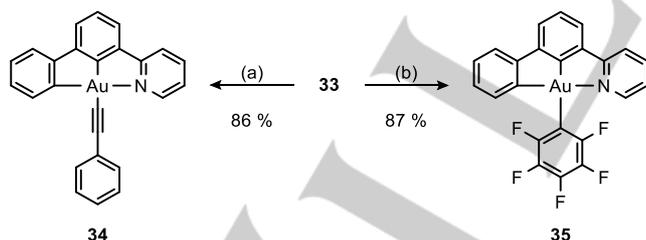
The diiodo biphenyl **26** was doubly lithiated and reacted with Me_2SnCl_2 to obtain the stannole **32**, which slowly decomposes upon chromatography; thus, analytically pure samples were obtained with moderate yields only (43 %). However, the crude stannole may be reacted with $\text{K}[\text{AuCl}_4]$ to obtain the non-palindromic $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{N})\text{Au}^{\text{III}}]$ complex **33** in 81 % yield (Scheme 8).



Scheme 8. Synthesis of $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{N})\text{Au}^{\text{III}}\text{Cl}]$ (**33**). Conditions: (a) 1) $^t\text{BuLi}$, Et_2O , $-78\text{ }^\circ\text{C}$, 2 h 2) Me_2SnCl_2 , $-78\text{ }^\circ\text{C}$ \rightarrow rt, 16 h; (b) $\text{K}[\text{AuCl}_4]$, MeCN , $0\text{ }^\circ\text{C}$ \rightarrow rt, 1 h.

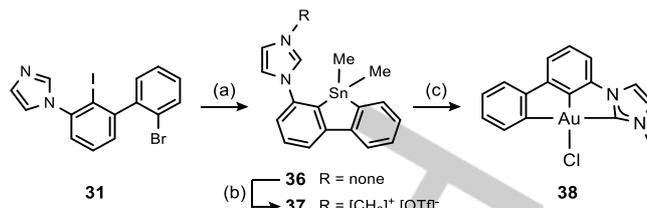
Complex **33** was obtained as colourless solid which dissolves readily in dichloromethane and toluene. However, after a couple of hours, it precipitates in form of yellow blocks which are suitable for X-ray diffraction analysis. Furthermore, **33** crystallizes from $\text{CH}_2\text{Cl}_2/n$ -hexane with one molecule of n -hexane in the unit cell (Figure S 9, SI). The yellow blocks only modestly dissolve in hot organic solvents, thus, NMR analysis was performed in $\text{DMSO-}d_6$ at $100\text{ }^\circ\text{C}$. Due to the poor solubility, chromatographic purification of **33** (instead of crystallization) results in notably reduced yields (62 %), however, the yellow blocks are fully suitable for further transformations. We note that **33** – if not already precipitated – decomposes in solution after three days forming elemental gold when exposed to light.

Thus, we reacted **33** with lithium phenylacetylide or $[(\text{MeCN})\text{AgC}_6\text{F}_5]^{[59]}$ to obtain the $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{N})\text{Au}^{\text{III}}]$ complexes **34** and **35** in 86 % and 87 % yield, respectively (Scheme 9).



Scheme 9. Synthesis of $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{N})\text{Au}^{\text{III}}]$ complexes. (a) LiCCPh , $\text{Et}_2\text{O}/\text{toluene}$ (1:1), rt, 3 h; (b) $[(\text{MeCN})\text{AgC}_6\text{F}_5]$, CH_2Cl_2 , rt, 16 h.

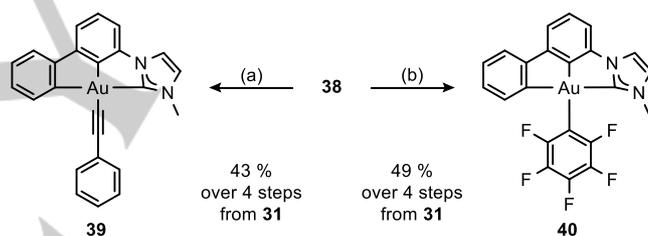
In a similar manner, we prepared stannole **36** and its methyl imidazolium salt **37** (Scheme 10).



Scheme 10. Synthesis of $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{C}')\text{Au}^{\text{III}}]$ complex **38**. Conditions: (a) 1) $^t\text{BuLi}$, Et_2O , $-78\text{ }^\circ\text{C}$, 2 h 2) Me_2SnCl_2 , $-78\text{ }^\circ\text{C}$ \rightarrow rt, 1 h; (b) MeOTf , CH_2Cl_2 , rt, 2 h. (c) $\text{K}[\text{AuCl}_4]$, MeCN , K_2CO_3 , rt, 2 h. The stannoles **36**, **37** and $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{C}')\text{Au}^{\text{III}}]$ complex **38** could not be isolated in pure form, thus, yields are not given.

Unfortunately, we were not able to obtain the stannoles **36** and **37** in pure form: Both are unstable against chromatography and did not crystallize. Nevertheless, we could prove their formation by NMR, APCI MS (**36**) and ESI MS (**37**) analyses of the crude reaction mixtures. The $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{C}')\text{Au}^{\text{III}}]$ complex **38** which we obtained by reacting **37** with $\text{K}[\text{AuCl}_4]$ in the presence of base rapidly decomposes in solution and in the presence of moisture too, which made the isolation of pure samples impossible as well.

However, crude **38** could be reacted with lithium phenylacetylide or $[(\text{MeCN})\text{AgC}_6\text{F}_5]^{[59]}$ to obtain the $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{C}')\text{Au}^{\text{III}}]$ complexes **39** and **40** in 43 % and 49 % yield (Scheme 11), respectively, over four steps starting from dihalobiphenyl **31**. The latter two complexes are stable towards moisture, air and chromatography.



Scheme 11. Synthesis of $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{C}')\text{Au}^{\text{III}}]$ complexes **39** and **40**. Conditions: (a) LiCCPh , $\text{Et}_2\text{O}/\text{toluene}$ (1:1), rt, 3 h; (b) $[(\text{MeCN})\text{AgC}_6\text{F}_5]$, CH_2Cl_2 , rt, 16 h.

Crystals suitable for X-ray diffraction analyses could be obtained from the pentafluorophenyl complexes **35** and **40** as well as the PhCC derivative **39** (Figure 1). Overall, the structural parameters of the investigated complexes are very similar. The Au–C17 bond of **39** has the same length as its $[(\text{C}^{\wedge}\text{C}^{\wedge}\text{N})\text{Au}^{\text{III}}]$ pendant,^[23] but the Au–C17 bond of **40** (206.2(14) pm) is about 5 pm shorter compared to the respective bond of its $(\text{C}^{\wedge}\text{C}^{\wedge}\text{N})$ congener **35** (Au–C18: 211.2(10) pm). The latter may be a result of the better π acceptor properties of the lateral carbene as compared to the pyridine donor-ligand. The molecules are rather closely packed in the solid state with distances between the planes spanned by the pincers ranging between 345 pm and 360 pm. The pentafluorophenyl complexes **35** and **40** are aligned in two different planes notably tilted against each other in the solid state, whereas the molecules of **39** are packed in a nearly parallel manner (Figure S 10, SI).

All complexes adopt structures with the aryl entities of the ancillary ligands tilted against the plane spanned by the donor atoms of the pincer ligand. They are not perpendicular aligned to the pincer's plane, however, the preference for the tilted arrangement is important with respect to photophysical considerations. Thus, for the following discussion, we want to rely on an idealized situation of perfectly perpendicular aryl entities. The structural feature of tilted/perpendicular aryl entities are also found for most palindromic $(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})$ analogues, either

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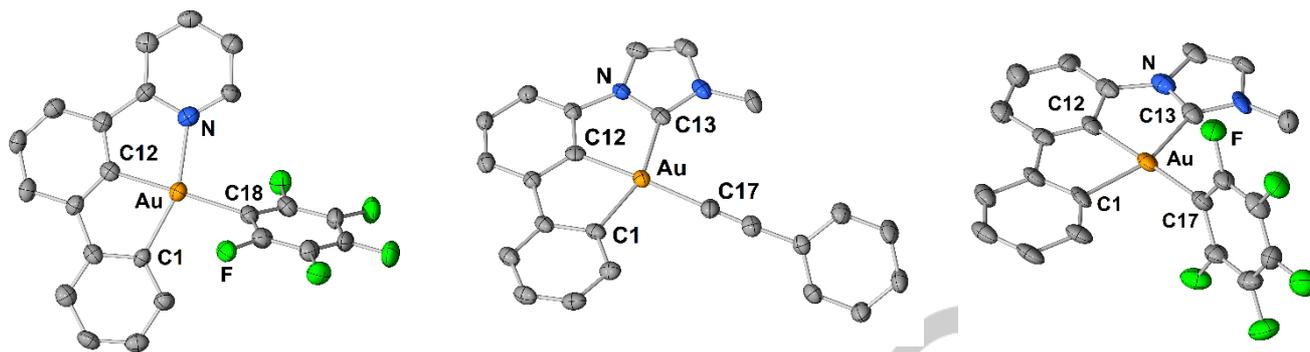


Figure 1. Solid state molecular structure of $[(C^A C^D)Au^{III}]$ complexes **35** (left), **39** (middle) and **40** (right). Thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Only one molecule of the asymmetric unit of **35** is shown. The asymmetric unit of **35** contains half a molecule hexane (not shown). Selected bond lengths (pm) and angles ($^\circ$), **35**: Au–C18 211.2 (10), Au–C1 209.4(10), Au–C12 200.7(10), Au–N 212.4(9), C1–Au–C12 78.9(4), C12–Au–N 80.1(4), C1–Au–C18–F 62.6(9); **39**: Au–C17 204.5(8), Au–C1 206.4(7), Au–C12 197.9(8), Au–C13 207.4(8), C1–Au–C12 79.6(4), C12–Au–C13 78.2(3); **40**: Au–C17 206.2(14), Au–C1 206.6(12), Au–C12 200.3(12), Au–C13 209.1(12), C1–Au–C12 78.9(6), C12–Au–C13 78.7(4), C1–Au–C17–C 97.9(1).

crystallographically^[10a] or by means of DFT calculations.^[10b] Nonetheless, the role of the tilted PhCC ligand is somewhat overlooked in the literature: Some (TD)DFT investigations are based on structures with a phenylethynyl ligand being in coplanar arrangement with the pincer moiety.^[8b, 25] This may be misleading with respect to the interpretation of photophysical properties. The $[(C^A N^A C)Au^{III}]$ motif belongs to the C_{2v} point group. Thus, $\pi_{CNC} \rightarrow \pi^*_{CNC}$ *intra* ligand transitions (IL) are of B_1 symmetry, i.e. dipole allowed. The same holds for the non-palindromic $[(C^A C^D)Au^{III}]$ structure, whose symmetry is C_s (A'). The character of $\pi_{ethynyl} \rightarrow \pi^*_{CNC}$ *inter* ligand transitions (LL'CT) depends on the orientation of the PhCC: In a coplanar arrangement, LL'CT is of A_1 symmetry (A' in C_s), i.e. an allowed transition; a tilted arrangement changes the $\pi \rightarrow \pi^*$ LL'CT to A_2 , which is dipole forbidden in C_{2v} . In C_s , the latter is dipole allowed in one direction (A''). The transition intensities are strongly affected by these symmetry properties, thus, being important for a sound discussion of photophysics.

Absorption and Emission Properties

Absorption and emission spectra of complexes **34**, **35**, **39** and **40** are shown in Figure 3. The photophysical properties are summarized in Table 1. We note that we did not observe any degradation of these complexes in the presence of light over the course of a couple of days neither in toluene nor in CH_2Cl_2 .

Like the $(C^A C^N)$ complexes reported by Nevado *et al.*,^[23] the absorption bands of **34** and **35** are blue shifted compared to the palindromic $(C^A N^A C)$ analogues.^[10a, 16] The vibronically structured bands between 330 and 280 nm ($\epsilon \sim 5000 - 15000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) with peak distances between 1200 cm^{-1} and 1400 cm^{-1} being typical for the pincer's ligand breathing modes probably arise from $\pi \rightarrow \pi^*$ IL transitions.^[10a, 23, 60] LL'CT transitions responsible for the first absorption bands can be ruled out because in this case the absorption profile of phenylethynyl (**34**) and pentafluorophenyl (**35**) derivate should considerably differ.

The $(C^A C^C')$ complexes **39** and **40** exhibit further blue-shifted absorptions. Obviously, the lateral carbene donor leads to electronic states shifted to higher energies compared to the $(C^A C^N)$ congeners. This is rooted in the higher energy levels of imidazole π^* orbitals^[61] as well as the stronger ligand field splitting causing higher lying gold centred d-orbitals. Thus, the absorption spectra of **39** and **40** clearly render the electron rich nature of the gold^{III} atom entailed by the $(C^A C^C')$ pincer.

The investigated complexes show intense luminescence in solution at room temperature with emission lifetimes in the micro- and sub-microsecond region indicating phosphorescence. The complexes are not emissive in the solid state maybe due to triplet-triplet annihilation^[62] facilitated by the close proximity of the complex molecules in the solid state: for instance, the distance of the planes spanned by the pincer ligand between two molecules of **40** in the solid state is found to be only 347 pm (Figure S 10, SI).

The emission pattern of all complexes is very similar. The vibronic structure with band distances of about 1300 cm^{-1} indicates pincer $\pi^* \rightarrow \pi$ centred transitions. Interestingly, the carbene donor does not alter the emission profile. The emission wavelengths of the $(C^A C^C')$ complexes **39** and **40** are negligibly shifted to higher energies. In addition, the PhCC or C_6F_5 ligands do not have any impact on the emission profile, thus, the transition is detached from these ligands. The emission spectra resemble the ones of other $[(C^A C^N)Au^{III}]$ ^[23] and $[(C^A N^A C)Au^{III}]$ complexes^[10, 16] as well as biphenyl-based $[(C^A C)Au^{III}]$ ^[63] or cyclometalated pyridine^[64] and carbene $[(C^A C')Au^{III}]$ complexes.^[29] Thus, the π orbital of the emissive $\pi \rightarrow \pi^*$ 3 IL state is almost exclusively centred at the (bi)phenyl unit of the respective pincer ligand.

Emission quantum yields Φ in dichloromethane solution at room temperature range between 3 and 10 % being higher than the yields of many $(C^A N^A C)$ analogues.^[10] Obviously, the quantum yields are not affected by the lateral donor of the pincer, but the ligand besides the pincer: The C_6F_5 substituted systems **39** and **40** phosphoresce up to three times more efficient than the PhCC analogues **34** and **35**. This is especially noteworthy, since the opposite finding was reported by Venkatesan and co-workers about the luminescence of cyclometalated $[(C^A N)Au(III)]$ ^[64] and $[(C^A C')Au(III)]$ ^[29] complexes. The authors found higher emission quantum yields for phenylethynyl substituted complexes than for pentafluorophenyl substituted ones. Furthermore, Bochmann and co-workers have shown for palindromic $[(C^A N^A C)Au^{III}]$ phenyl complexes that the phosphorescence quantum yield increases when going from pentafluorophenyl $[(C^A N^A C)Au^{III}C_6F_5]$ ^[65] to less fluorinated variants like $[(C^A N^A C)Au^{III}C_6F_4H]$ ($\Phi = 0.6 \%$) and $[(C^A N^A C)Au^{III}C_6H_4F]$ ($\Phi = 1.3 \%$).^[16] This may be understood from the weaker donor strength of (per)fluorinated aryl ligands resulting in smaller ligand field splitting of the gold(III) atom. In contrast, the PhCC ligand is a sufficiently strong donor to enable phosphorescence.^[10, 66] Obviously, the non-palindromic pincer motifs reported in the present study overcompensate the weaker

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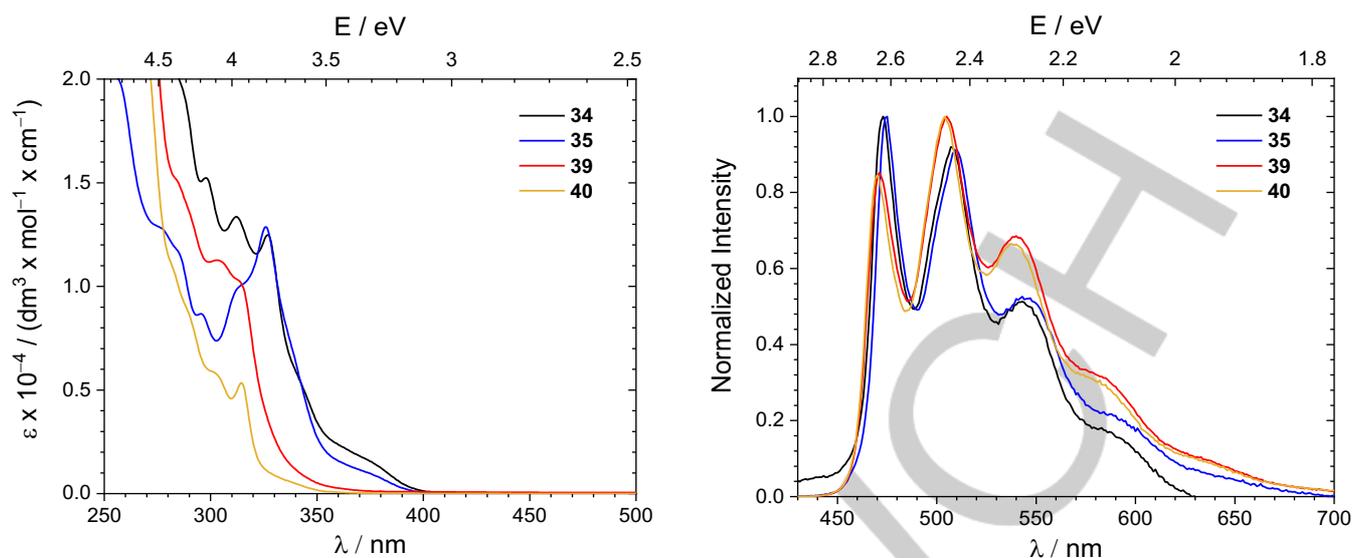


Figure 3. Left: UV/Vis spectra of $[(C^{\wedge}C^{\wedge}N)Au^{III}CCPh]$ (**34**), $[(C^{\wedge}C^{\wedge}N)Au^{III}C_6F_5]$ (**35**), $[(C^{\wedge}C^{\wedge}C)Au^{III}CCPh]$ (**39**) and $[(C^{\wedge}C^{\wedge}C)Au^{III}C_6F_5]$ (**40**). Right: Emission spectra in solution. All spectra were recorded at 293 K in dry and degassed CH_2Cl_2 . The excitation wavelength was chosen to match the respective first absorption maximum.

Table 1. Photophysical data of gold complexes **34**, **35**, **39** and **40** in solution^[a] at 293 K.

complex	λ_{abs} nm	ϵ $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	λ_{em} nm	Φ_p [b]	τ_p [c] μs	k_p [d] 10^5 s^{-1}	k_{nr} [e] 10^5 s^{-1}
34	298, 312, 327, 376	1.52, 1.34, 1.25, 0.15	473, 507, 543, 588	0.03	0.8	0.38	12.13
35	278, 285, 295, 314, 326, 370	1.27, 1.16, 0.87, 1.00, 1.29, 0.12	475, 410, 546, 589	0.09	4.1	0.22	2.22
39	284, 303, 314	1.51, 1.13, 1.02	471, 505, 540, 581	0.03	1.0	0.30	0.97
40	302, 314, 336	0.58, 0.54, 0.06	470, 504, 539, 582	0.10	0.5	2.0	1.80

[a] Dried and deoxygenated dichloromethane. [b] Absolute quantum yields, determined by use of an integrating sphere ($c = 10^{-4} \text{ mol dm}^{-3}$). [c] Phosphorescence lifetime. [d] Rate constant phosphorescence, $k_p = \Phi_p/\tau_p$. [e] Rate constant radiationless relaxation, $k_{nr} = (1 - \Phi_p)/\tau_p$.

ligand-field splitting, i.e. the ligand field splitting of **35** and **40** is strong enough despite the weak pentafluorophenyl donor. However, this does not explain why the latter complexes outperform the phenylethynyl **34** and **39** regarding phosphorescence quantum yields. In order to shed some more light on these aspects, we performed quantum chemical calculations.

Quantum Chemical Calculations

To investigate the phosphorescence properties of the four complexes, and especially the different quantum yields observed for the differently substituted complexes, GW/Bethe-Salpeter and time-dependent density-functional theory (TD-DFT) calculations using the TPSSh functional were performed at the quasi-relativistic two-component level including spin-orbit coupling.

Absorption spectra were found to be in good agreement with experimental data. When optimizing the first excited triplet state, we find a shift of the emission lines for all four complexes to a nearly constant value. Calculated 0–0 triplet emission energies are found at 619 nm/2.00 eV (**34**), 620 nm/2.00 eV (**35**), 623 nm/1.99 eV (**39**), and 626 nm/1.98 eV (**40**) while a natural-transition-orbital (NTO) analysis confirms the $\pi \leftarrow \pi^*$ triplet intra-ligand (3IL) character of this excitation as described in the previous section. The TD-DFT (TPSSh) and GW/BSE

calculations are in good mutual agreement. GW/BSE excitation and emission energies are slightly red shifted by approx. 0.15 eV.

Even though there is good agreement between the predicted and observed spectra, the quantum yield needs further investigation, as the difference between the PhCC and C_6F_5 -ligated systems cannot be explained by the emission spectra

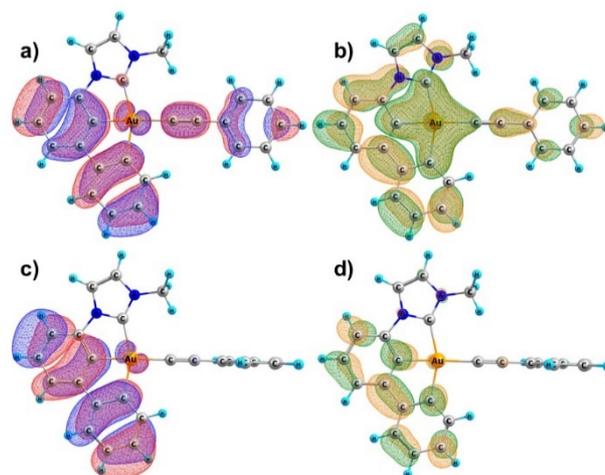


Figure 2. Natural transition orbitals of the hole (red/blue) - particle (green/orange) pairs of the first triplet excitation in the planar (a,b) and tilted (c,d) configuration of complex **39**.

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alone. A main difference between these complexes is given by their ability to rotate about the Au-C axis. For the phenylethynyl complexes **39** and **34**, we have obtained rotational barriers of only 2.0 kJ/mol and 1.1 kJ/mol, respectively, and therefore assume a rapid rotation of the ligand at room temperature, as it was done by Yam *et al.*^[8b] Due to steric hindrance, however, no rotation is observed for the bulkier pentafluorophenyl ligand, and a stable transition-state geometry could not be located. In the vicinity of the transition-state geometry, where the phenylethynyl and pincer ligands are nearly coplanar, the first triplet excited state changes its character from *intra-* (IL) to *inter-*ligand charge-transfer (LL'CT, Figure 2). This allows for an efficient pathway to release the excess energy of the excited state, suppressing the phosphorescence of complexes **34** and **39**. In the tilted geometry, this LL'CT state is also present, but only as a higher-lying excited state. Therefore, for the bulkier -C₆F₅ ligand, this non-radiative relaxation pathway is closed as the overlap between the π systems is never sufficiently high at any reasonable geometry to yield a significant transition moment dipole.

But even for the PhCC complexes, the overall transition probability is still not high in the coplanar configuration, explaining why only diminished emission quantum yields are observed instead of full quenching. The different transition dipole moment's magnitude for tilted (LL'CT: A'') and coplanar geometry (LL'CT: A') nicely correspond to a qualitative picture based on group theory considerations.

We note that rotation is also possible for alkyl ligands, for which high phosphorescence quantum yields have been observed.^[12] However, the non-radiative LL'CT relaxation pathway does not exist for alkyl ligands due to the lack of an adjacent π system.

For a detailed overview of the methods used, excitation and emission spectra including spin orbit coupling, and a detailed analysis of the character of the corresponding relevant excitations, we refer to the SI.

Conclusion

In summary, we have described the development of a synthetic access to donor substituted 2,2'-dihalo biphenyls which are suitable pre-ligands for the preparation of highly luminescent [(C[^]C[^]D)Au^{III}] (D = pyridine, NHC) complexes by means of a transmetalation sequence. This synthetic methodology expands the possibilities for gold(III) pincer complex synthesis and constitutes a complementary variant to the approach of Nevado and co-workers. In addition, we report on the first example of a pincer complex comprising two anionic, sp²-hybridized and one neutral L-type carbon donors.

We investigated the prepared pincer complexes by means of X-ray diffraction analysis, UV/Vis and emission spectroscopy and supported our experimental findings by quantum chemical calculations on the TD-DFT and GW/Bethe-Salpeter level of theories. We could show the outstanding electronic properties of the non-palindromic pincer motif compared to its palindromic congeners. A strong ligand field splitting is reflected in blue shifted absorptions and high emission quantum yields in solution at room temperature. In addition, we could clarify non-radiative relaxation pathways and support our description by group theoretical arguments.

Upcoming studies currently performed in our group are focused on modified procedures to introduce functional groups into the pincer moieties to systematically investigate and tune the chemical and photophysical properties of derived complexes. Furthermore, the dihalobiphenyls are examined with regard to their applicability to other transition metal complexes and main group elements probably opening up a rich chemistry with possible applications in catalytic, photophysical/-chemical, materials or pharmaceutical applications.

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Keywords: pincer ligand • luminescence • gold complex • photophysics • quantum chemistry

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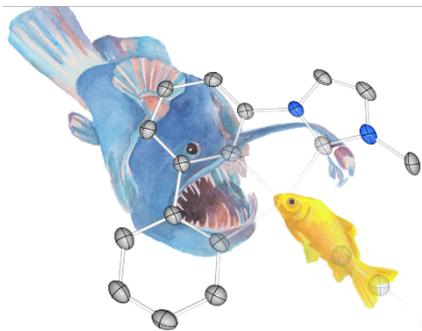
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- [65] The pentafluorophenyl derivative shows luminescence with a quantum yield of about 1 %, however, this is rooted in a fluorescence as clearly seen from a small Stokes shift, emission lifetimes in the nanosecond region and different vibronic bands.
- [66] The stronger donor properties of phenylethynyl compared to pentafluorophenyl is also reflected in a blue shifted absorption of the [(C^N^C)Au^{III}] phenylethynyl complex compared to its C₆F₅ pendant.

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Capture the Gold(fish)! Donor-substituted dihalobiphenyls are suitable pre-ligands for the preparation of luminescent, non-palindromic $[(C^*C^*D)Au^{III}]$ complexes with a lateral pyridine or carbene donor. Like an anglerfish's rod enmeshes its prey, the lateral donor tunes the gold's electronic properties which is held by the rigid biphenyl mouth. Synthesis, spectroscopy and quantum chemistry draw a comprehensive picture about the new complexes prepared.

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