

## Coordination Chemistry

# Synthesis of New Donor-Substituted Biphenyls: Pre-ligands for Highly Luminescent (C<sup>∧</sup>C<sup>∧</sup>D) Gold(III) Pincer Complexes

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**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[AuCl<sub>4</sub>] forming non-palindromic [(C<sup>∧</sup>C<sup>∧</sup>D)Au<sup>III</sup>] 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 sp<sup>2</sup> and one carbenic carbon donor. The [(C<sup>∧</sup>C<sup>∧</sup>D)Au<sup>III</sup>] complexes show intense phosphorescence in solution at room temperature. We discuss the de-

veloped multistep 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)<sup>[1]</sup> are far less studied in the context of phosphorescent organic light-emitting diodes (PhOLEDs)<sup>[2]</sup> than systems incorporating other heavy metals, for example, iridium(III),<sup>[3]</sup> ruthenium(II)<sup>[4]</sup> or platinum(II).<sup>[5]</sup> However, there is increasing interest in gold(III)-based systems mainly employing a 2,6-diphenylpyridine (C<sup>∧</sup>N<sup>∧</sup>C)-based pincer ligand.<sup>[6]</sup> The (C<sup>∧</sup>N<sup>∧</sup>C) pincer diminishes radiationless relaxation pathways of excited complexes due to its rigid nature<sup>[7]</sup> 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.<sup>[8]</sup>

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

We note that highly emissive tetradentate Au<sup>III</sup> complexes reported only recently may outperform many tridentate systems in this regard,<sup>[15]</sup> however, complexes with tetradentate ligands are less attractive for possible applications in chemical or catalytic transformations because all coordination sites of the central Au<sup>III</sup> atom are occupied. That [(C<sup>∧</sup>N<sup>∧</sup>C)Au<sup>III</sup>] 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<sup>∧</sup>N<sup>∧</sup>C)Au<sup>III</sup>] hydroxides<sup>[16]</sup> and hydrides.<sup>[17]</sup> In addition, they prepared [(C<sup>∧</sup>N<sup>∧</sup>C)Au<sup>III</sup>] olefin<sup>[18]</sup> and alkyne complexes<sup>[19]</sup> thereby showing the suitability of these complexes for C–C bond forming reactions. Finally, some [(C<sup>∧</sup>N<sup>∧</sup>C)Au<sup>III</sup>] complexes are investigated in the realm of anticancer drug research<sup>[20]</sup> with a very recent study about photo-activatable cytotoxic [(C<sup>∧</sup>N<sup>∧</sup>C)Au<sup>III</sup>] hydrides.<sup>[21]</sup>

The (C<sup>∧</sup>N<sup>∧</sup>C) motif is introduced by treating a mono-cyclo-metalated mercury compound like **1** with gold(III) salts (Scheme 1). In 2015, Nevado and co-workers reported on the

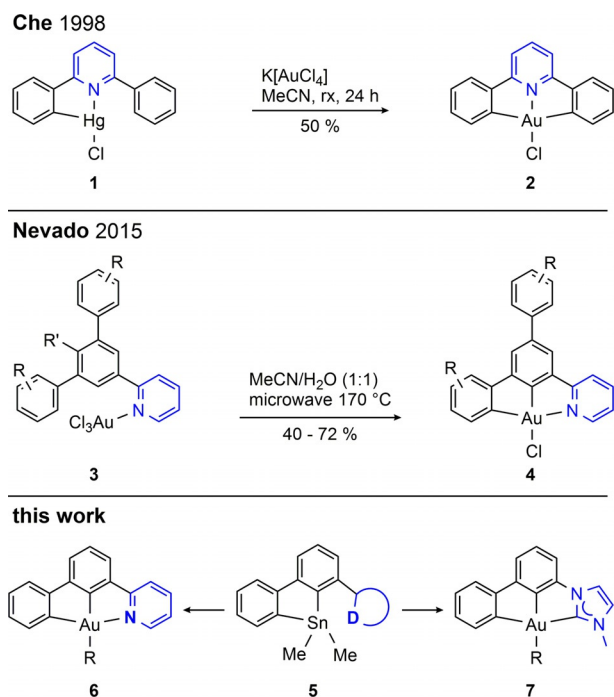
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**Scheme 1.** Preparation of palindromic ( $C^{\wedge}N^{\wedge}C$ ) and non-palindromic ( $C^{\wedge}C^{\wedge}N$ )  $Au^{III}$  complexes reported in the literature and the synthetic approach presented in this study. D: Donor.

synthesis of the non-palindromic<sup>[22]</sup> [ $C^{\wedge}C^{\wedge}N$ ] $Au^{III}$  analogue which exhibits exchanged positions of the central pyridine ring and one lateral phenyl donor (**4** in Scheme 1).<sup>[23]</sup> 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 nonpalindromic ( $C^{\wedge}C^{\wedge}N$ ) pincer was shown to exhibit high emission quantum yields making its gold(III) complexes particularly interesting for OLED fabrication.<sup>[24]</sup> This was assigned to a higher ligand field splitting of these complexes compared to the palindromic ( $C^{\wedge}N^{\wedge}C$ ) congeners which was investigated by TDDFT.<sup>[8b,25]</sup>

The central phenyl donor of the ( $C^{\wedge}C^{\wedge}N$ ) ligand exhibits a stronger *trans* influence than the ( $C^{\wedge}N^{\wedge}C$ )'s central pyridine. This made the preparation of stable  $Au^{III}$  fluorides<sup>[23]</sup> and formates<sup>[26]</sup> possible and finds expression in notably different NMR shifts of the respective hydrides.<sup>[17b]</sup> Moreover, the *trans* influence affects the complexes' reactivity: [ $C^{\wedge}C^{\wedge}N$ ] $Au^{III}$  carboxylates favour thermal decarbonylation reactions<sup>[27]</sup> whereas the ( $C^{\wedge}N^{\wedge}C$ ) based carboxylates show elimination of  $CO_2$ .<sup>[28]</sup>

There are no reports in the literature on gold(III) pincer complexes with two aryl donors and a third donor other than pyridine ( $D=N$ ), for example, carbene. However, bidentate, ( $C^{\wedge}C'$ ) cyclometalated ( $C'=NHC$  carbon donor)  $Au^{III}$  complexes were reported by von Arx et al.<sup>[29]</sup> and Crespo et al.<sup>[30]</sup>

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 ap-

proach constitutes a complementary variant of the synthesis developed by Nevado and co-workers to prepare non-palindromic [ $C^{\wedge}C^{\wedge}N$ ] $Au^{III}$  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,<sup>[31]</sup> thereby showing the utility of these methods in the field of photophysics and photochemistry.

## Results and Discussion

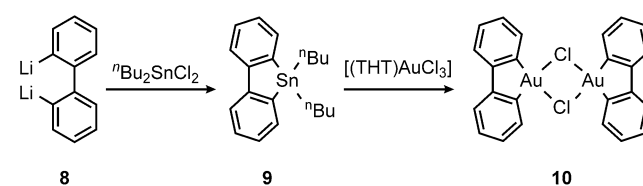
### Retrosynthetic considerations

Our synthetic approach for the preparation of non-palindromic [ $C^{\wedge}C^{\wedge}D$ ] $Au^{III}$  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).<sup>[32]</sup>

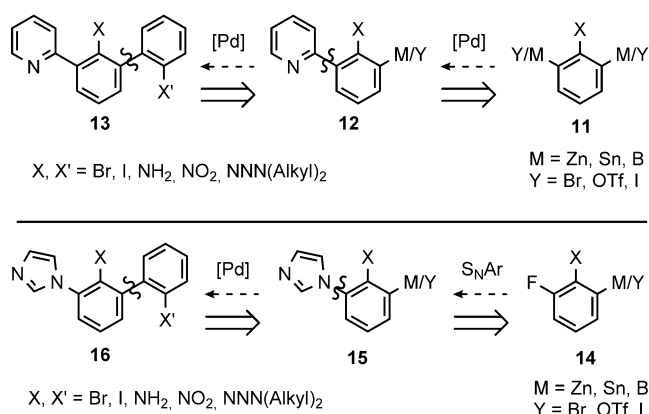
Direct transmetalation of dilithiobiphenyls to  $Au^{III}$  is only possible for very electron-poor biphenyls like perfluorinated ones<sup>[33]</sup> or special  $Au^{III}$  precursors<sup>[34]</sup> due to the tendency of  $Au^{III}$  to become reduced by organometallic reagents. Besides the findings of Toste,<sup>[35]</sup> Bourissou<sup>[36]</sup> and Bertrand<sup>[37]</sup> 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.<sup>[34,38]</sup> Thus, we anticipated the corresponding 4-substituted stannoles **5** would be equally useful for the preparation of non-palindromic ( $C^{\wedge}C^{\wedge}D$ ) complexes of gold.

Dilithiobiphenyl **8** may be prepared by reaction of biphenyl with two equivalents of  $nBuLi$ ,<sup>[39]</sup> 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, that is, anilines ( $X, X'=NH_2$ ), nitrobenzenes ( $X, X'=NO_2$ ) or triazines ( $X, X'=$



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



**Scheme 3.** Retrosynthetic aspects of the preparation of dihalobiphenyls with pyridine (C<sup>∧</sup>C<sup>∧</sup>N) (**13**) or NHC (C<sup>∧</sup>C<sup>∧</sup>C') (**16**) donor. [Pd]: Pd catalysed C–C cross coupling.

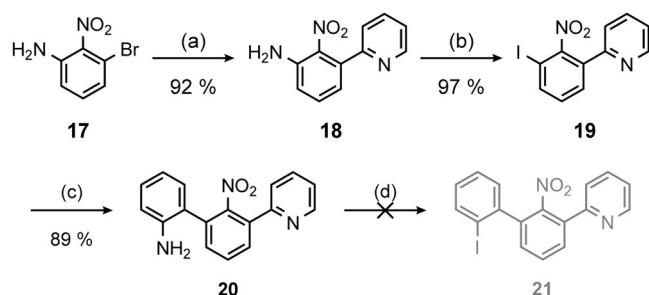
NNR<sub>2</sub>), by means of Sandmeyer-type reactions,<sup>[40]</sup> eventually after reduction of NO<sub>2</sub>. The latter must be performed after building the core pincer structure to ensure selectivity of the C–C cross couplings. Phenylpyridine **12** might be obtained by C–C cross coupling as 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**.

### Pre-ligand synthesis

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

Iodide **19** was then coupled with 2-(aminophenyl)boronic acid by means of a Suzuki–Miyaura coupling.<sup>[42,43]</sup> Unfortunately, diazotization-iodination of **20** failed, although there are reports on the successful diazotization-iodination of 2'-nitro-2-phenyl-anilines (Scheme 4).<sup>[44]</sup>

Beside the classical variant using HCl/NaNO<sub>2</sub>/KI, we also tried DMSO-based reagents<sup>[45]</sup> or modifications employing CuBr<sub>2</sub>.<sup>[46]</sup>



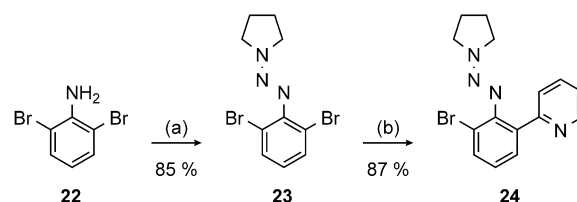
**Scheme 4.** Attempt to obtain biphenyl **21**. Conditions: (a) 2-(Tributylstannyl)pyridine, LiCl, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (4 mol %), xylene, rx, 6 h; (b) 1) HCl, NaNO<sub>2</sub>, H<sub>2</sub>O, 0 °C, 30 min 2) KI, 0 °C → rt, 12 h; (c) 2-(aminophenyl)boronic acid, K<sub>3</sub>PO<sub>4</sub>, XPhos Pd G3 (3 mol %),<sup>[42]</sup> 1,4-dioxane/H<sub>2</sub>O (4:1), 70 °C, 90 min; (d) 1) HCl, NaNO<sub>2</sub>, H<sub>2</sub>O, 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 S9, Supporting Information).

Substitution of NH<sub>2</sub> by Me<sub>3</sub>Sn according to a diazotization-stannylation protocol led only to unidentified decomposition products.<sup>[47]</sup> Attempts to isolate the corresponding diazonium salt employing H[BF<sub>4</sub>]/NaNO<sub>2</sub> or [NO][PF<sub>6</sub>] 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.<sup>[48]</sup> We also directly introduced 2-bromophenyl to **19**, however, this approach had unacceptably low yields (Section S 1.2, Supporting Information).

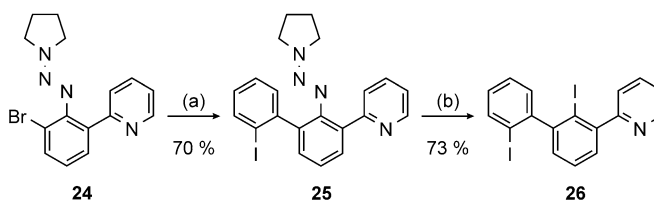
We then turned our attention to a different approach based on the triazene **23** as key structure which was described by Knochel and co-workers in the context of carbazole syntheses.<sup>[49]</sup> Magnesiumation using *turbo*-Grignard,<sup>[50]</sup> subsequent transmetalation with ZnBr<sub>2</sub> and reaction with 2-bromopyridine by means of a Negishi-coupling<sup>[40,51]</sup> gave **24** in 87% isolated yield (Scheme 5).

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

The latter was only successful under meticulous temperature control: **24** was lithiated at –98 °C with precooled (–78 °C) *n*BuLi in hexanes and subsequently transmetalated with ZnBr<sub>2</sub> to obtain a Negishi-reagent suitable for coupling with 1,2-diiodobenzene. Prior to that, we tried magnesiumation 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 Rieke<sup>[52]</sup> or in the presence of LiCl.<sup>[53]</sup> This is probably rooted in the electron-rich nature of **24** in contrast to the substrates reported by the group of Knoch-



**Scheme 5.** Synthesis of triazene **24**. Conditions: (a) 1) HCl, NaNO<sub>2</sub>, H<sub>2</sub>O, 0 °C, 30 min. 2) K<sub>2</sub>CO<sub>3</sub>, pyrrolidine, MeCN, 0 °C → rt, 2 h; (b) 1) *i*PrMgCl·LiCl, THF, –40 °C → –15 °C, 4 h. 2) ZnBr<sub>2</sub>, –20 °C → 5 °C, 1 h. 3) 2-bromopyridine, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (10 mol %), reflux, 16 h.

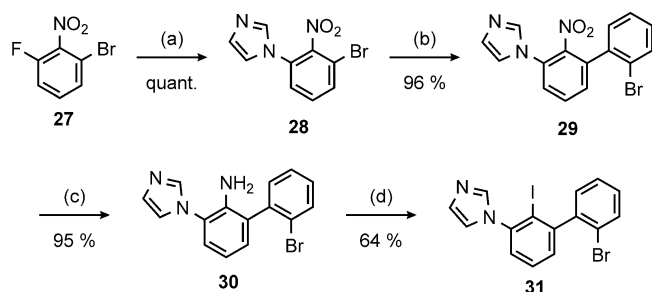


**Scheme 6.** Synthesis of diiodo biphenyl **26**. Conditions: (a) 1) *n*BuLi (pre-cooled to –78 °C), –100 °C, 90 min. 2) 1 M ZnBr<sub>2</sub> in THF (pre-cooled to –78 °C), –100 °C → –78 °C, 1 h, rt, 1 h. 3) 1,2-diiodobenzene, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (5 mol %), rx, 16 h. (b) Amberlyst 15<sup>®</sup>, KI, MeCN, 70 °C, 10 min. The structure of **25** in the solid state could be determined by X-ray diffraction analysis (Figure S9, Supporting Information).

el<sup>[53a]</sup> who used only electron-deficient triazenes for direct zinc insertions. Treating **24** with elementary magnesium led only to decomposition products even in the presence of ZnCl<sub>2</sub>. Consequently, we tried to lithiate **24** and transmetalate with ZnBr<sub>2</sub>. Under standard conditions (*n*BuLi or two eq. *t*BuLi –78 °C) we detected only decomposition products, maybe due to decomposition by  $\alpha$ -deprotonation at the pyrrolidine which is known to readily happen at higher temperatures.<sup>[54]</sup>

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

For the preparation of a (C<sup>^</sup>C<sup>^</sup>C<sup>^</sup>) pre-ligand we started with commercially available 1-bromo-3-fluoro-2-nitrobenzene (**27**) (Scheme 7).



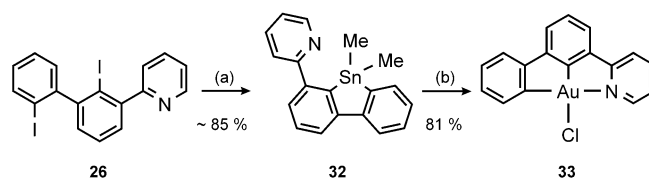
**Scheme 7.** Synthesis of (C<sup>^</sup>C<sup>^</sup>C<sup>^</sup>) pre-ligand **31**. Conditions: (a) Imidazole, NaOH, DMSO, rt, 2 h; (b) 2-bromophenyl boronic acid, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (5 mol%), K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O (2:1), rx, 18 h; (c) Fe, EtOH/HOAc (1:1), rx, 3 h; (d) 1) 6 M HCl, NaNO<sub>2</sub>, 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 S9, Supporting Information).

After introduction of imidazole by means of a nucleophilic aromatic substitution<sup>[58]</sup> (**28**), we introduced 2-bromophenyl (**29**) and subsequently reduced the nitro group to obtain the aniline **30**. The latter tends to cyclize with triazene formation (Section S 2.1, Supporting Information), however, under strongly acidic conditions the dihalobiphenyl **31** can be obtained in 64% yield, corresponding to a good overall 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 prepared on a 10 to 20 g scale.

### Complex synthesis and characterization

The diiodo biphenyl **26** was doubly lithiated and treated with Me<sub>2</sub>SnCl<sub>2</sub> 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 K[AuCl<sub>4</sub>] to obtain the non-palindromic [(C<sup>^</sup>C<sup>^</sup>N)Au<sup>III</sup>] complex **33** in 81% yield (Scheme 8).



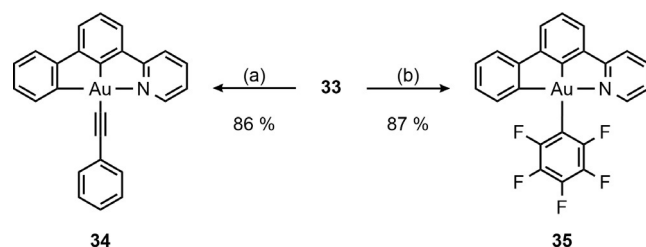
**Scheme 8.** Synthesis of [(C<sup>^</sup>C<sup>^</sup>N)Au<sup>III</sup>] (**33**). Conditions: (a) 1) *t*BuLi, Et<sub>2</sub>O, –78 °C, 2 h. 2) Me<sub>2</sub>SnCl<sub>2</sub>, –78 °C → rt, 16 h; (b) K[AuCl<sub>4</sub>], MeCN, 0 °C → rt, 1 h.

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 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane with one molecule of *n*-hexane in the unit cell (Figure S9, Supporting Information). The yellow blocks only modestly dissolve in hot organic solvents, thus, NMR analysis was performed in [D<sub>6</sub>]DMSO at 100 °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.

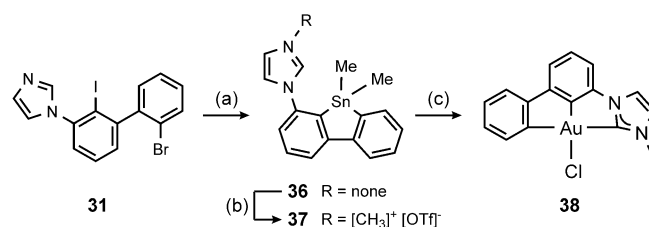
Thus, we treated **33** with lithium phenylacetylide or [(MeCN)AgC<sub>6</sub>F<sub>5</sub>]<sup>[59]</sup> to obtain the [(C<sup>^</sup>C<sup>^</sup>N)Au<sup>III</sup>] complexes **34** and **35** in 86% and 87% yield, respectively (Scheme 9).

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

Unfortunately, we were not able to obtain the stannoles **36** and **37** in pure form: Both are unstable during chromatogra-



**Scheme 9.** Synthesis of [(C<sup>^</sup>C<sup>^</sup>N)Au<sup>III</sup>] complexes. (a) LiCCPh, Et<sub>2</sub>O/toluene (1:1), rt, 3 h; (b) [(MeCN)AgC<sub>6</sub>F<sub>5</sub>], CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h.



**Scheme 10.** Synthesis of [(C<sup>^</sup>C<sup>^</sup>C<sup>^</sup>C<sup>^</sup>)Au<sup>III</sup>] complex **38**. Conditions: (a) 1) *t*BuLi, Et<sub>2</sub>O, –78 °C, 2 h. 2) Me<sub>2</sub>SnCl<sub>2</sub>, –78 °C → rt, 1 h; (b) MeOTf, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h. (c) K[AuCl<sub>4</sub>], MeCN, K<sub>2</sub>CO<sub>3</sub>, rt, 2 h. The stannoles **36**, **37** and [(C<sup>^</sup>C<sup>^</sup>C<sup>^</sup>C<sup>^</sup>)Au<sup>III</sup>] complex **38** could not be isolated in pure form, thus, yields are not given.

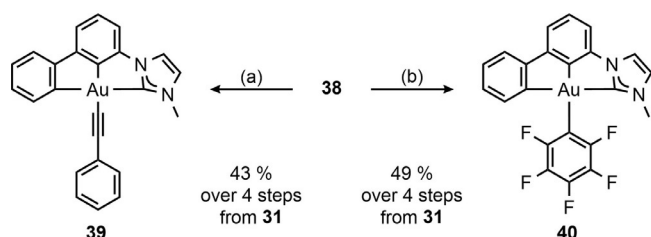
phy and did not crystallize. Nevertheless, we could prove their formation by NMR spectroscopy, APCI MS (**36**) and ESI MS (**37**) analyses of the crude reaction mixtures. The  $[(C^{\wedge}C^{\wedge}C)Au^{III}]$  complex **38** which we obtained by treating **37** with  $K[AuCl_4]$  in the presence 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 treated with lithium phenylacetylide or  $[(MeCN)AgC_6F_5]^{[59]}$  to obtain the  $[(C^{\wedge}C^{\wedge}C)Au^{III}]$  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.

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  $[(C^{\wedge}C^{\wedge}N)Au^{III}]$  pendant,<sup>[23]</sup> but the Au–C17 bond of **40** (206.2(14) pm) is about 5 pm shorter compared to the respective bond of its  $(C^{\wedge}C^{\wedge}N)$  congener **35** (Au–C18: 211.2(10) pm). The latter may be a result of the better  $\pi$  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 S10, Supporting Information).

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  $(C^{\wedge}N^{\wedge}C)$  analogues, either crystallographically<sup>[10a]</sup> or by means of DFT calculations.<sup>[10b]</sup> 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.<sup>[8b,25]</sup> This may be misleading with respect to the interpretation of photophysical properties. The  $[(C^{\wedge}N^{\wedge}C)Au^{III}]$  motif belongs to the  $C_{2v}$  point group. Thus,  $\pi_{CNC} \rightarrow \pi^*_{CNC}$  intraligand transitions (IL) are of  $B_1$  symmetry, that is, dipole allowed. The same holds for the non-palindromic  $[(C^{\wedge}C^{\wedge}D)Au^{III}]$  structure, whose symmetry is  $C_s$  ( $A'$ ). The character of  $\pi_{ethynyl} \rightarrow \pi^*_{CNC}$  interligand transitions (LL'CT) depends on the orientation of the PhCC: In a coplanar arrangement, LL'CT is of  $A_1$  symmetry ( $A'$  in  $C_s$ ), that is, 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.

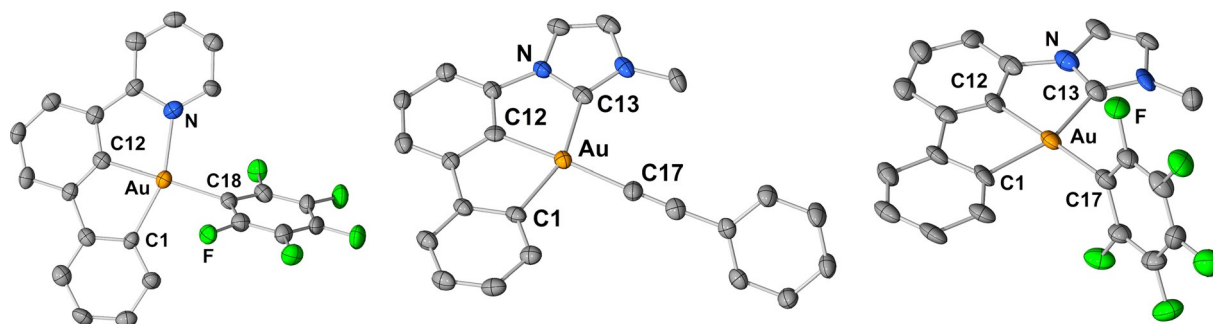


**Scheme 11.** Synthesis of  $[(C^{\wedge}C^{\wedge}C)Au^{III}]$  complexes **39** and **40**. Conditions: (a) LiCCPh, Et<sub>2</sub>O/toluene (1:1), rt, 3 h; (b)  $[(MeCN)AgC_6F_5]$ , CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h.

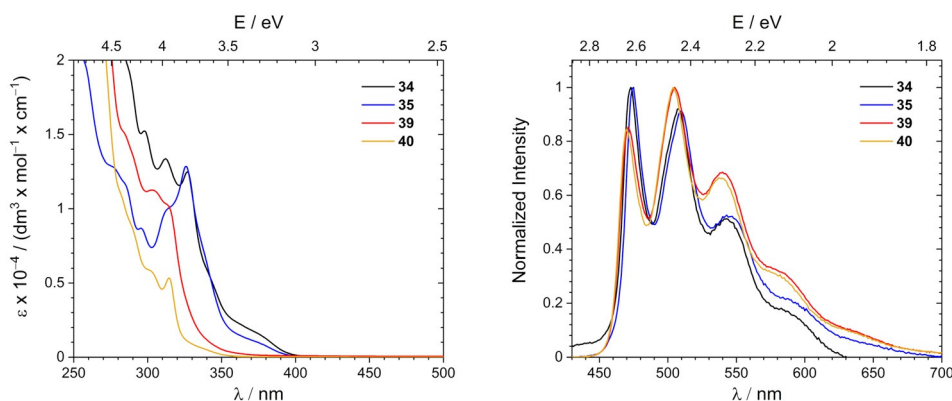
### Absorption and emission properties

Absorption and emission spectra of complexes **34**, **35**, **39** and **40** are shown in Figure 2. 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<sub>2</sub>Cl<sub>2</sub>.

Like the  $(C^{\wedge}C^{\wedge}N)$  complexes reported by Nevado et al.,<sup>[23]</sup> the absorption bands of **34** and **35** are blue shifted compared to the palindromic  $(C^{\wedge}N^{\wedge}C)$  analogues.<sup>[10a,16]</sup> The vibronically



**Figure 1.** Solid state molecular structure of  $[(C^{\wedge}C^{\wedge}D)Au^{III}]$  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).



**Figure 2.** Left: UV/Vis spectra of [(C<sup>^</sup>^N)Au<sup>III</sup>CCPh] (**34**), [(C<sup>^</sup>^N)Au<sup>III</sup>C<sub>6</sub>F<sub>5</sub>] (**35**), [(C<sup>^</sup>^C')Au<sup>III</sup>CCPh] (**39**) and [(C<sup>^</sup>^C')Au<sup>III</sup>C<sub>6</sub>F<sub>5</sub>] (**40**). Right: Emission spectra in solution. All spectra were recorded at 293 K in dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. 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<sup>[a]</sup> at 293 K.

Complex	$\lambda_{\text{abs}}$ nm	$\epsilon$ $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{em}}$ nm	$\Phi_p$ <sup>[b]</sup>	$\tau_p$ <sup>[c]</sup> $\mu\text{s}$	$k_p$ <sup>[d]</sup> $10^5 \text{ s}^{-1}$	$k_{nr}$ <sup>[e]</sup> $10^5 \text{ s}^{-1}$
<b>34</b>	298, 312, 327, 376	1.52, 1.34, 1.25, 0.15	473, 507, 543, 588	0.03	0.8	0.38	12.13
<b>35</b>	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
<b>39</b>	284, 303, 314	1.51, 1.13, 1.02	471, 505, 540, 581	0.03	1.0	0.30	0.97
<b>40</b>	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,  $k_{nr} = (1 - \Phi_p) / \tau_p$ .

structured bands between 330 and 280 nm ( $\epsilon \approx 5000$ – $15000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) with peak distances between  $1200 \text{ cm}^{-1}$  and  $1400 \text{ cm}^{-1}$  being typical for the pincer's ligand breathing modes probably arise from  $\pi \rightarrow \pi^*$  IL transitions.<sup>[10a,23,60]</sup> LLCT transitions responsible for the first absorption bands can be ruled out because in this case the absorption profile of phenylethynyl (**34**) and pentafluorophenyl (**35**) derivative should considerably differ.

The (C<sup>^</sup>^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<sup>^</sup>^N) congeners. This is rooted in the higher energy levels of imidazole  $\pi^*$  orbitals<sup>[61]</sup> 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<sup>III</sup> atom entailed by the (C<sup>^</sup>^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<sup>[62]</sup> 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 S10, Supporting Information).

The emission pattern of all complexes is very similar. The vibronic structure with band distances of about  $1300 \text{ cm}^{-1}$  indicates pincer  $\pi^* \rightarrow \pi$  centred transitions. Interestingly, the carbene donor does not alter the emission profile. The emission

wavelengths of the (C<sup>^</sup>^C') complexes **39** and **40** are negligibly shifted to higher energies. In addition, the PhCC or C<sub>6</sub>F<sub>5</sub> 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<sup>^</sup>^N)Au<sup>III</sup>]<sup>[23]</sup> and [(C<sup>^</sup>^N^C)Au<sup>III</sup>] complexes<sup>[10,16]</sup> as well as biphenyl-based [(C<sup>^</sup>^C)Au<sup>III</sup>]<sup>[63]</sup> or cyclometalated pyridine<sup>[64]</sup> and carbene [(C<sup>^</sup>^C')Au<sup>III</sup>] complexes.<sup>[29]</sup> Thus, the  $\pi$  orbital of the emissive  $\pi \rightarrow \pi^*$  IL state is almost exclusively centred at the (b)iphenyl unit of the respective pincer ligand.

Emission quantum yields  $\Phi$  in dichloromethane solution at room temperature range between 3 and 10% being higher than the yields of many (C<sup>^</sup>^N^C) analogues.<sup>[10]</sup> Obviously, the quantum yields are not affected by the lateral donor of the pincer, but the ligand besides the pincer: The C<sub>6</sub>F<sub>5</sub> 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<sup>^</sup>^N)Au<sup>III</sup>]<sup>[64]</sup> and [(C<sup>^</sup>^C')Au<sup>III</sup>]<sup>[29]</sup> 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<sup>^</sup>^N^C)Au<sup>III</sup>] phenyl complexes that the phosphorescence quantum yield increases when going from pentafluorophenyl [(C<sup>^</sup>^N^C)Au<sup>III</sup>C<sub>6</sub>F<sub>5</sub>]<sup>[65]</sup> to less fluorinated variants like [(C<sup>^</sup>^N^C)Au<sup>III</sup>C<sub>6</sub>F<sub>4</sub>H] ( $\Phi = 0.6\%$ ) and [(C<sup>^</sup>^N^C)Au<sup>III</sup>C<sub>6</sub>H<sub>4</sub>F] ( $\Phi = 1.3\%$ ).<sup>[16]</sup> This may be understood from the weaker donor strength of (per)fluorinated aryl ligands resulting in smaller

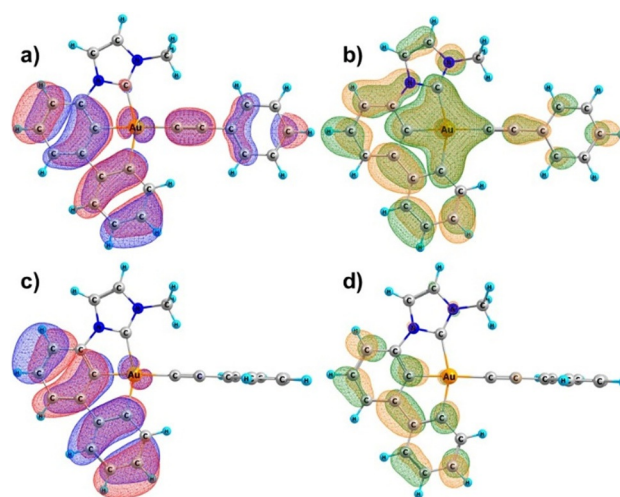
ligand field splitting of the gold(III) atom. In contrast, the PhCC ligand is a sufficiently strong donor to enable phosphorescence.<sup>[10,66]</sup> Obviously, the non-palindromic pincer motifs reported in the present study overcompensate the weaker ligand-field splitting, that is, the ligand field 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  $0 \leftarrow 0$  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 intraligand ( $^3$ IL) 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 approximately 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 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  $2.0 \text{ kJ mol}^{-1}$  and  $1.1 \text{ kJ mol}^{-1}$ , respectively, and therefore assume a rapid rotation of the ligand at room temperature, as it was done by Yam et al.<sup>[8b]</sup> 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 interligand charge-transfer (LL'CT, Figure 3). 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  $-C_6F_5$  ligand, this non-radiative relaxation pathway is closed as the overlap between the  $\pi$  systems is never sufficiently high at any reasonable geometry to yield a significant transition dipole moment.



**Figure 3.** 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**.

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.<sup>[12]</sup> However, the non-radiative LL'CT relaxation pathway does not exist for alkyl ligands due to the lack of an adjacent  $\pi$  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 Supporting Information.

### Conclusions

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  $[(C^{\wedge}C^{\wedge}D)Au^{III}]$  ( $D = \text{pyridine, NHC}$ ) 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,  $sp^2$ -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 being 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 catalysis, photophysics and -chemistry as well as material or pharmaceutical sciences.

## Crystallographic data

Deposition Numbers 1986483, 1986486, 2009470, 2009476, 2009473, 2009475, 2009471, 2009477, 1986481, 2009474, 2009472, 1991871 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** gold complexes · luminescence · photophysics · pincer ligand · quantum chemistry

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