

Environmentally Friendly, Photochemical Access to $[N^{\wedge}C^{\wedge}N]Au^{III}$ Pincer Complexes By Oxidative Addition

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Abstract: Starting from commercially available $DMSAuCl$ and diazonium salts, cationic $[N^{\wedge}C^{\wedge}N]Au^{III}$ complexes were synthesized in a selective, photosensitizer-free, photochemical reaction by irradiation with blue LED light. This new protocol represents the first easy synthesis of these types of pincer complexes in moderate to excellent yield starting from a readily available gold(I) precursor with nitrogen as the only by-product. Owing to the disadvantages of known protocols, especially the toxicity in the case of a transmetalation with mercury or the necessity for a mostly twofold excess of a gold precursor, this method offers an attractive alternative towards this kind of gold(III) complexes. In addition, the first arylated $[N^{\wedge}C^{\wedge}N]Au^{III}$ pincer complex was synthesized by using this technology.

Pincer ligands have many extraordinary features. The good control of the reactivity at the metal center due to a fixed, predetermined ligand geometry and their thermal stability, which results from the strong coordination of the donor atoms to the metal center, enables a manifold of applications in homogenous catalysis, especially for industry.^[1–3] Due to the square planar geometry of gold(III) complexes, tridentate pincer ligands are also very common for these species. But, while neutral $[C^{\wedge}N^{\wedge}C]gold(III)$ complexes are well studied, cationic $[N^{\wedge}C^{\wedge}N]$ complexes were investigated much less. This might be

attributed to the difficult synthetic access which is underlined by the fact that so far only six examples of $[N^{\wedge}C^{\wedge}N]Au(III)$ pincer complexes are known, even though this ligand class is widely explored for other d^8 transition metal complexes.^[4,5]

Pritchard and coworkers reported the first example of an $[N^{\wedge}C^{\wedge}N]Au(III)$ pincer compound in 1996. In a transmetalation reaction, a nitrogen-containing pincer ligand was transferred to $NaAuCl_4$ as precursor from the corresponding monodentate organomercury(II) substrate (Scheme 1a)).^[6] The scope was limited to a single compound and the usage of highly toxic mercury was necessary. Some years later, van Koten synthesized the same complex possessing chloride as a counter anion. In this protocol a triphenylphosphine-gold(I)-aryl-complex was used as the transmetalation reagent, which could be regenerated by the lithiated $[N^{\wedge}C^{\wedge}N]$ compound (Scheme 1b). Nevertheless, this recycling process is accompanied by stoichiometric amounts of salt waste and the need of moisture-sensitive organometallic reagents.^[7] In 2009, Manassero published a synthetic protocol, which was based on a direct C,H-activation of a pincer ligand with $H[AuCl_4]$ as the metal source in a buffered combination of acetic acid and five equivalents of sodium hydrogen carbonate. After two days, the corresponding cyclometallated five-membered ring product was isolated (Scheme 1c)).^[8] Still this protocol has the drawback that two equivalents of the gold source are essential. The same group, together with Gosh, also developed a method for six-membered $[N^{\wedge}C^{\wedge}N]gold(III)$ pincer complexes. In this case a direct C–H-activation strategy did not lead to the desired complex, instead a transmetalation reaction from a mercury(II) precursor to gold(III) chloride trihydrate was effective, with the same drawbacks as the already mentioned process (Scheme 1d)).^[9] In 2013, Wenger and coworkers published $Au(III)$ complexes with benzimidazole ligands. Neither a direct complexation nor a transmetalation starting from the corresponding silver(I) source led to the desired product and like in most of the other cases, a toxic mercury(II) precursor enabled the synthesis of $Au(III)$ complexes bearing a 1,3-bis(1-hexyl-2'-benzimidazolyl)-benzene backbone (Scheme 1e)).^[10] Like in the cases mentioned above, the stoichiometric generation of toxic mercury waste for these protocols is a huge drawback. In 2017, Chiniforoshan published a synthetic protocol which was also based on a direct C,H-activation of a benzimidazole- $[N^{\wedge}C^{\wedge}N]$ -pincer system. By refluxing the ligand with potassium tetrachloroaurate in glacial acetic acid, the complex could be isolated by slow addition of an excess of lithium hexafluorophosphate (Scheme 1f)).^[11,12] In contrast to all other processes, this protocol only depends on the use of only one equivalent of the gold precursor but still it

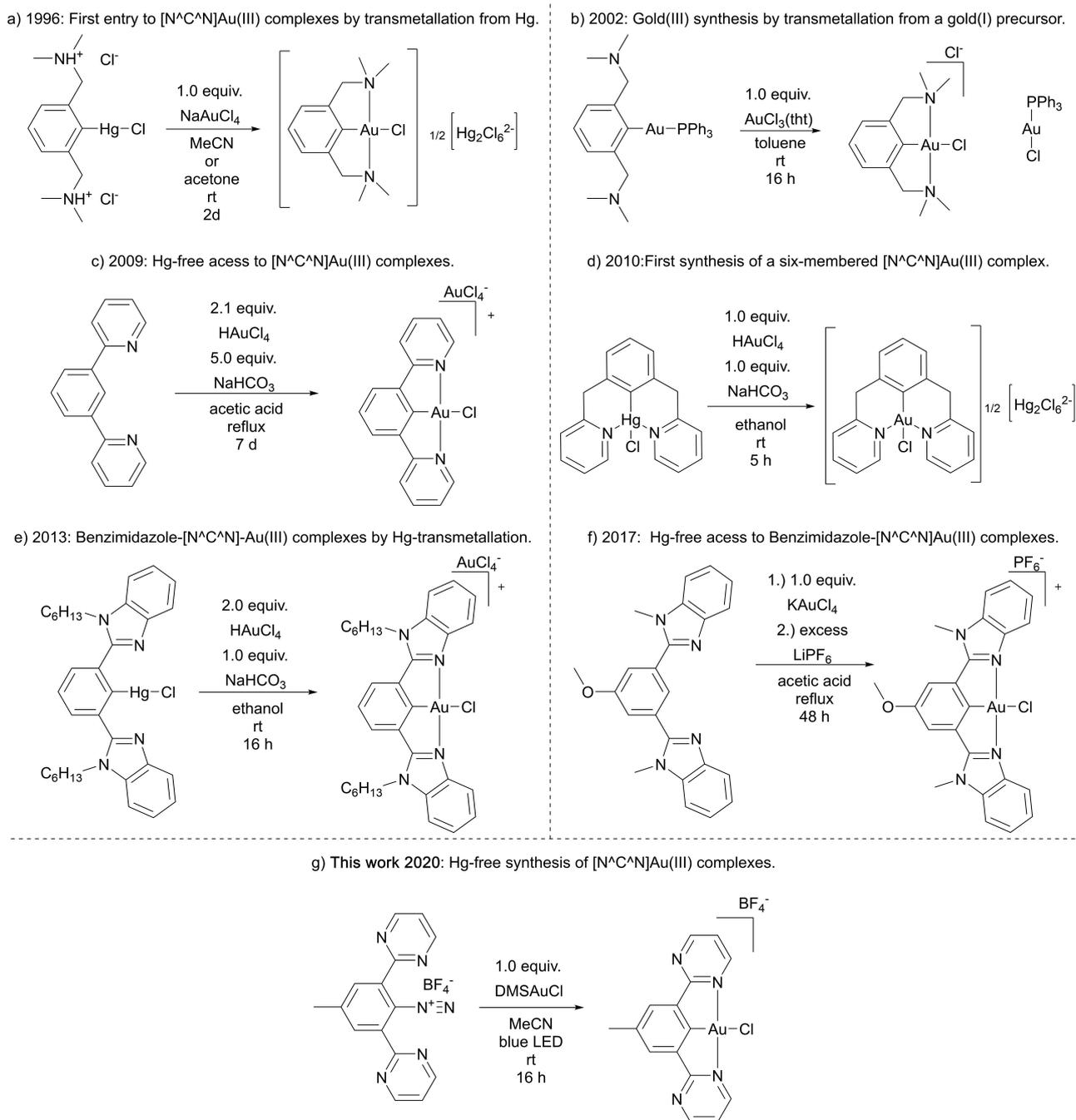
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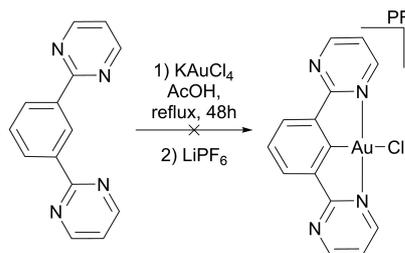
Scheme 1. Overview of all existing [N⁺C⁻N]Au(III) complexes and their synthesis.

was limited to only one single complex which only differs by a methoxy-group from the already reported example from Scheme 1e. In summary, this type of gold complexes is still limited to only a few specific examples and either highly toxic organomercury(II) compounds as transmetallation reagents or mostly a twofold excess of a gold precursor limit the synthetic potential of these approaches. We herein report an attractive alternative, the first easy, waste-minimized and environmentally friendly, mercury-free synthesis of cationic [N⁺C⁻N]Au(III)Cl complexes starting from diazonium salts and DMSAuCl by

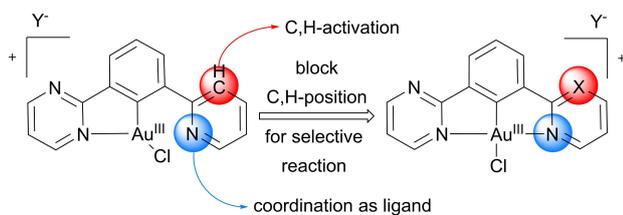
oxidative addition with nitrogen as the only byproduct (Scheme 1g).

First, we tested the N⁺C⁻N-ligand system with a pyrimidine backbone under the reaction conditions of Chiniforoshan (Scheme 2a). But, after 48 hours, no gold(III) complex could be isolated, probably because of the higher basicity of pyrimidine than benzimidazole. With this knowledge in hand, we envisioned that the reactivity of diazonium salts, in analogy to earlier works of our group, might enable an entry to this class of complexes.^[13,14] In addition, we recently developed a

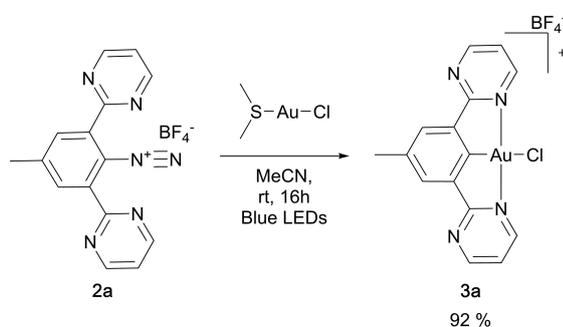
a) Conversion of Pyrimidine-Ligand with protocol of Chiniforoshan.



b) Possible reaction pathways during the complex formation.



c) Successful complex synthesis with envisioned strategy.



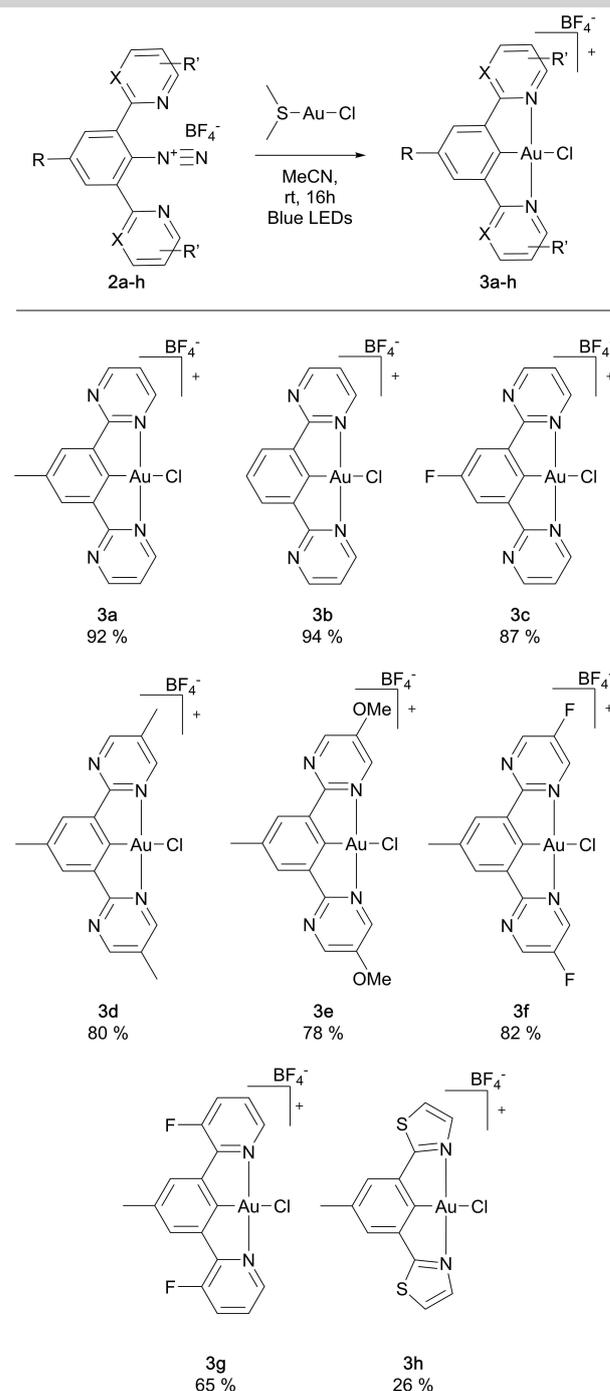
Scheme 2. First experiments.

mercury-free synthesis of $[C^{\wedge}N^{\wedge}C]Au(III)$ pincer complexes based on an oxidative addition, C,H-activation cascade by using DMSAu(I) chloride and diazonium salts as precursors.^[15] We considered pyrimidine as ligand for this reactivity pattern as advantageous because two equal positions are available for N-coordination while in the case of a pyridine ligand, the reactive gold intermediate could undergo a competing C,H-activation of the aryl CH-bond to form a $[N^{\wedge}C^{\wedge}C]Au$ complex as undesired side reaction (Scheme 2b). This was confirmed by the reaction with pyridine as ligand. In this case the crude 1H NMR of the reaction mixture showed an unselective reaction, most probably due to the formation of different types of complexes.

By using the symmetrical pyrimidine-substituted 4-methyl-2,6-di(pyrimidin-2-yl)benzenediazonium salt **2a**, the success of this strategy could be demonstrated and the desired product **3a** was formed very smoothly in 92% yield (Scheme 2c).

With these insights in hand, various arene diazonium salts were converted (Table 1). First, we varied the backbone of the diazonium salt. In all cases, the gold(III) complex was isolated in excellent yield and an electron-donating (92%, **3a**), an unsubstituted (94%, **3b**) and an electron-deficient (84%, **3c**) backbone were suitable for the complex synthesis. Next, we turned our focus on the expansion of the substrate scope regarding

Table 1. Synthesis of five-membered $[N^{\wedge}C^{\wedge}N]Au(III)$ complexes.^[a,b]



[a]: Reaction conditions: diazonium salt (**2a–h**, 100 μ mol), DMSAu(I)Cl (100 μ mol) in acetonitrile (1 mL, 0.1 M) were reacted at rt under irradiation with blue LEDs; [b]: Isolated yields.

different pyrimidine units in combination with the methyl-substituted backbone. A methyl group in the 5-position of the pyrimidine linker delivered a good result of 80% (**3d**). The more electron-rich methoxy group (78%, **3e**) and an electron-deficient 5-fluoro-pyrimidine as ligand (82%, **3f**) were almost equally efficient which indicates that the effect of the electronic

properties of the pyrimidine substituent on the synthetic efficiency is only low.

For the latter compound, an X-ray crystal structure analysis was conducted, which unambiguously verifies the connectivity of the complex (Figure 1 – left). Non-symmetrical ligands other than pyrimidines were tested next. In the case of a pyridine ring with a blocking fluor atom in 3-position, the yield of **3g** dropped to a moderate 65 % (see Figure 1 – right for the solid-state molecular structure). The structure very nicely shows the pyridine ring, in which a fluorine atom blocks each possible second C,H-activation position. Also an unsymmetrical thiazole unit delivered the $[N^{\wedge}C^{\wedge}N]Au(III)$ complex **3h** in a yield of 26 %. The low efficiency in this case may result from additional coordination of the sulfur atom or competing side-reactions at sulfur.

Next, we were curious about a possible replacement of the chloride ligand attached to the gold center. Different possibilities of substitution at the isolated $[N^{\wedge}C^{\wedge}N]Au(III)Cl$ complexes were evaluated but neither a Sonogashira reaction nor a reaction with phenyllithium were effective. The approach starting from cationic $IMesAuBF_4$ with the diazonium salt, generated a deep orange, glittering solid after isolation, but the measured NMR showed an unselective reaction. To our delight, the reaction between diazonium salt **2c** and dimethyl sulfide

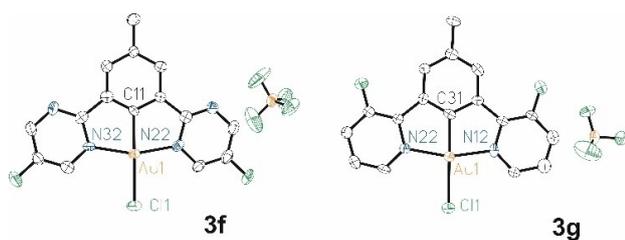
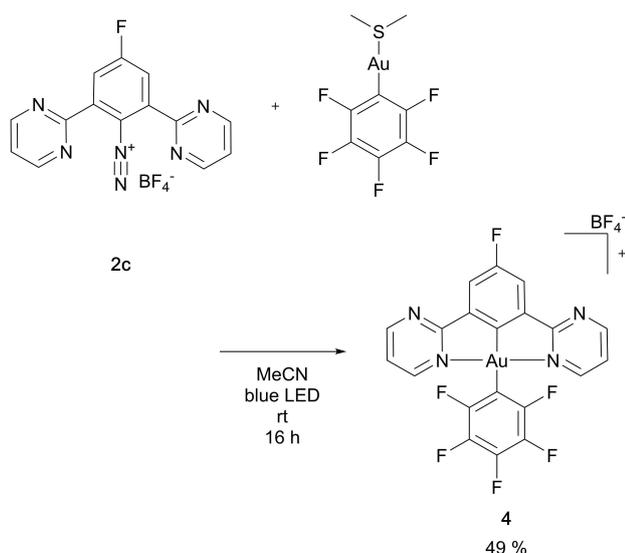


Figure 1. Solid-state molecular structure of **3f** (left) and **3g** (right). Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.^[16]



Scheme 3. First synthesis of arylated $[N^{\wedge}C^{\wedge}N]Au(III)$ compound.

gold(I)pentafluorobenzene^[17] delivered the first cationic, arylated $[N^{\wedge}C^{\wedge}N]Au(III)$ complex **4**, which was isolated in a yield of 49% as an intensive red solid (Scheme 3).

The structure of $[N^{\wedge}C^{\wedge}N]Au(III)C_6F_5$ complex **4** could be unambiguously established by X-ray diffraction analysis (Figure 2). Selected bond distances and angles of **3f**, **3g**, **4** and the literature known $[P^{\wedge}C^{\wedge}N^{\wedge}C]AuCl$ example (see Supporting Information) are displayed in Table 2.

The observed gold – carbon distances of compound **4** has the same length than the literature reported gold – nitrogen bond of the $[C^{\wedge}N^{\wedge}C]AuCl$ complex and is slightly longer than the gold–carbon bonds in complexes **3f** and **3g**, respectively. The quite similar electronegativity of gold and carbon results in a highly covalent gold–carbon bond.^[5] The respective angles between the trans aryl carbon atoms of the literature known complex with 163.3° is almost equal with the compared trans nitrogen atoms of complexes **3f**, **3g** and **4** (range 160° – 162°). However, it is important to note that the respective angle between C(11)–Au(1)–C(41) of compound **4** with 176° is significantly deviated from a linear axis, while the other mentioned complexes reach almost 180° along this corresponding axis. The aryl ring rotating out of the plane is probably responsible for the difference in angle and in addition it prevents from π – π interactions which are very common for the square planar geometry of gold(III) complexes (Figure 2).

A plausible mechanism, which is in line with our previous work is illustrated and described (Scheme 4).^[13,14,18] After irradiation of the diazonium salt **1** with blue light LED, an aryl radical is formed. Oxidative addition and a single electron transfer from

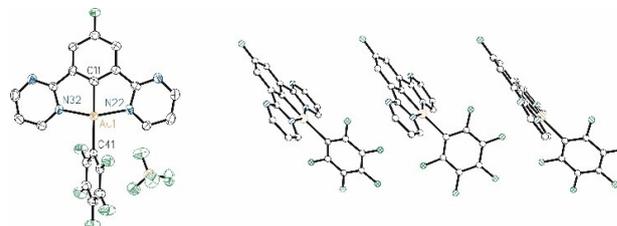
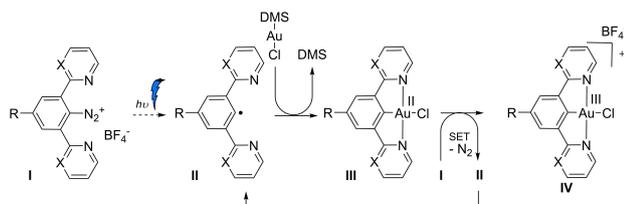


Figure 2. X-Ray structure of **4**. Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for a clarity.^[16]

Table 2. Selected bond lengths and angles.			
Complex 3f			
Au(1)–C(11)	1.96 Å	Au(1)–Cl(1)	2.35 Å
N(32)–Au(1)–N(22)	160°	C(11)–Au(1)–Cl(1)	179°
Complex 3g			
Au(1)–C(31)	1.94 Å	Au(1)–Cl(1)	2.33 Å
N(22)–Au(1)–N(12)	162°	C(31)–Au(1)–Cl(1)	180°
Complex 4			
Au(1)–C(11)	1.98 Å	Au(1)–C(41)	2.10 Å
N(32)–Au(1)–N(22)	160°	C(11)–Au(1)–C(41)	176°
Literature Known Complex $[P^{\wedge}C^{\wedge}N^{\wedge}C]AuCl$^[15]			
Au–N	1.98 Å	Au–Cl	2.28 Å
C–Au–C	163°	N–Au–Cl	179°



Scheme 4. Proposed reaction mechanism.

the Au(II) center to another diazonium salt leads to cationic gold(III) intermediate III, which directly gets coordinated from the pyrimidine ring to generate $[(\text{NCN})\text{Au}(\text{III})\text{Cl}][\text{BF}_4]$ complex IV.

In summary, a very easy, photosensitizer-free,^[19,20] blue LED-mediated oxidative addition of diazonium salts to $\text{DMSAu}(\text{I})\text{Cl}$ for the synthesis of cationic $[\text{N}^{\wedge}\text{C}^{\wedge}\text{N}]\text{Au}(\text{III})$ complexes bearing tetrafluoroborate as counteranion was developed. This environmentally friendly, mercury-free protocol allows a smooth entry to a yet underexplored ligand class with nitrogen as the only byproduct. By starting from dimethyl sulfide gold(I) pentafluorobenzene, the first arylated $[\text{N}^{\wedge}\text{C}^{\wedge}\text{N}]\text{Au}(\text{III})$ organometallic compound could be isolated and identified by X-ray single-crystal structure analysis. This atom economic protocol may deliver the method of choice for synthesizing these yet underexplored targets and therefore contribute to evaluations of potential biological activity or applications in material science.

Experimental Section

In an oven-dried Pyrex-Vial benzenediazonium salt (1.0 equiv) and $\text{DMS-gold}(\text{I})\text{chloride}$ (1.0 equiv) were added. The atmosphere was changed via three cycles of vacuum and purging with N_2 . Then dry acetonitrile (0.1 M) was added via syringe and the reaction mixture was transferred into a blue LED photoreactor and irradiated at rt for 16 h. Then diethyl ether (10 mL) were added and a precipitate was formed which was collected via filtration. The solid was washed with diethyl ether (3×10 mL) and dried *in vacuo*.

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Conflict of Interest

The authors declare no conflict of interest.

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