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Halide Exchange

Synthesis, Characterization, and Reactivity of Cyclometalated Gold(III) Dihalide Complexes in *Aqua Regia*

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Dedicated to Dr. Jean-René Hamon, wonderful friend and dedicated chemist, on the occasion of his 65th birthday.

Abstract: A range of N,C-chelated, cyclometalated gold(III) complexes Au(ppy^R)X_2 have been prepared and characterized by spectroscopic, crystallographic, and computational means. Here, ppy^H is 2-phenylpyridine dicarboxylic acid (series **1**), ppy^{Et} is diethyl 2-phenylpyridine dicarboxylate (series **2**), and X is trifluoroacetate OAc^F (**a**), Cl (**b**), Br (**c**), or I (**d**) anion. The dihalo complexes **1b-d** and **2b-d** are obtained when Au(ppy^R)(OAc^F)$_2$ (**1a** and **2a**) are treated with HNO_3/HX mixtures (*aqua regia*^{X}). Good to high yields are obtained with short reaction times (< 30 min) and simple work-up. Notably, the strongly acidic medium does not cause protolytic cleavage of the Au–C or Au–N bonds in the chelate, nor is ester hydrolysis of complexes **2b-d** seen. Ethylene inserts into an Au–O bond of **1a** and **1b**, and the resulting trifluoroacetoxyethyl–Au complexes can be further elaborated in *aqua regia* without cleavage of the two Au–C bonds in the molecule. Facile, mutual halide exchange reactions between complexes with different halides (**1b** and **1d**, **1c** and **1d**) were observed and led to formation of mixed-halide complexes Au(ppy^H)(X)(Y). These exchange reactions occurred with complete stereoselectivity. The stereoisomer produced was the one expected based on the relative *trans* influence of the halides (I > Br > Cl), i.e. the highest *trans* influence halide was located *trans* to N which is the lowest *trans* influence end of the chelate. These thermodynamic preferences were also investigated by DFT computations.

Introduction

In recent years, gold has paved its way in the field of catalysis with its unique reactivity patterns and the high activity and robustness of many developed Au(I) and Au(III) catalysts.[1–6] In the field of homogeneous gold catalysis, the development and use of Au(I) catalysts has dominated over Au(III), in part due to the superior availability and stability of Au(I) complexes compared to Au(III) ones. More recently, development of Au(III) systems have gained momentum due to, in part, advances of versatile and robust synthetic procedures.[5]

The most commonly used Au(III) complexes are cyclometalated square-planar complexes with chelating and pincer ligands.[7–12] Chelated, square planar Au(N^C) complexes where N^C is a cyclometalated phenylpyridine (*ppy*) ligand scaffold have been extensively studied, and offer the possibility of decorating the aromatic rings with a variety of desirable substituents. Such cyclometalated complexes have proven to be active catalysts for a range of reactions, including aromatic addition to vinyl ketones,[13] AAA-coupling reactions,[14,15] and heterocycle syntheses.[16–18]

Despite the increasing interest in cyclometalated *ppy*-Au(III) complexes, their synthesis was for some time hampered by the need to use stoichiometric transition metal reagents to effect cyclometalation, such as Ag(I) salts for halide abstraction or transmetalation via toxic Hg(I/II) complexes.[19–21] Constable and co-workers reported the preparation of Au(*ppy*)Cl_2 by direct auration in MeCN/water in 80 % yield.[22] Their approach appears to work well in particular with electron-donating substituents at the pyridine moiety, whereas lower yields are reported with electron donating groups.[23] This substituent limitation is not experienced with our microwave heating method, which also obviates the need for transmetalation.[24] Recently, we reported that the microwave protocol works well with carboxylate-functionalized *ppy* derivatives, which makes the Au(III) complexes amenable to incorporation into metal-organic frameworks (MOFs).[25] The microwave approach has been demonstrated thus far to be particularly useful for the preparation of ligand-based substituted derivatives of Au(*ppy*)Cl_2 and Au(*ppy*)(OAc^F)$_2$ (Scheme 1; OAc^F = trifluoroacetate).

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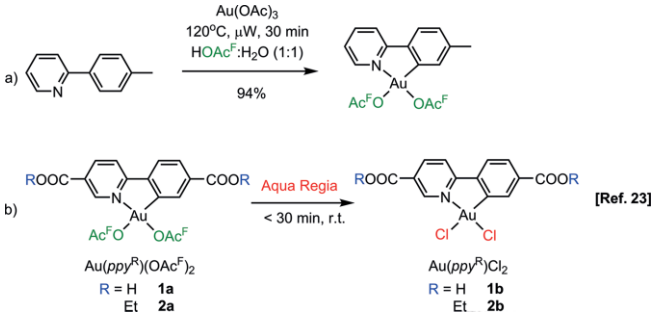


Scheme 1.

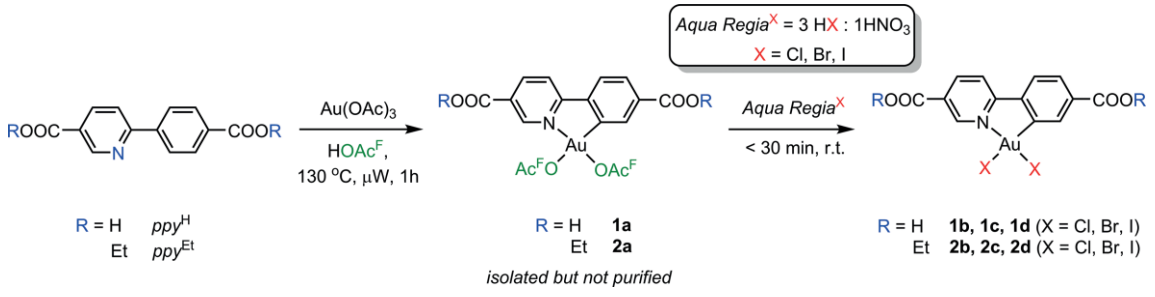
The most abundant class of cyclometalated Au(III) complexes involves those with two chloro ligands bonded to the Au(III) center.[10] The reactivity of the chlorides has been studied in details and their derivatization by substitution reactions have been exploited.[21] Preparative methods for the substitution of other X-type ligands for Cl in cyclometalated Au(III) dichloride complexes include the obvious reactions with anionic ligands, including Br^- and I^-, in aqueous media or acetone.[26] Occasionally, the occurrence of side reactions together with low yields present practical challenges in synthesis and isolation of the substitution products.[21] Furthermore, the presence of small quantities of NMR-silent Au nanoparticles or colloids can represent an obstacle in purification of the complexes. We envisioned, and have recently demonstrated,[25,27,28] that this challenge might be overcome by using *aqua regia* – that is of course well known for its ability to dissolve metallic gold[29] – as a reaction medium.

The use of *aqua regia* as a solvent for preparative organometallic chemistry is limited. The constituents HNO_3 and HCl are abundant and inexpensive, but toxicity, safety, and corrosion issues render the medium less attractive. It is worth mentioning, however, that highly acidic and corrosive media enabled Periana and co-worker's progress in the development of Pt-catalyzed hydrocarbon activation and functionalization in fuming sulfuric acid media.[30–33] The reports for *aqua regia* usage include oxidation of Au(I) pyrazolato complexes to their Au(III) analogues[34–36] and our more recent account of the oxidation of an electron poor, ferrocenyl-substituted Au(NHC)Cl complex.[27] Recently, we explored the use of *aqua regia* as reaction medium and oxidation agent to oxidize various more conventional Au(NHC)Cl complexes to Au(NHC)Cl_3 analogues.[28] Finally, and most relevant to this contribution, we described the successful use of *aqua regia* in the synthesis of **1b** and **2b** from the bis(trifluoroacetate) complexes **1a** and **2a** (Scheme 1b). It was demonstrated that complexes **1b** could be installed in a UiO-67 MOF framework.[25] Here, we report further reactivity of **1a–b** and **2a–b** in strongly acidic media, including *aqua regia*. Bromo and iodo analogues are prepared. Ethylene inserts into an Au–O bond of **1a** and **1b**, and the resulting trifluoroacetoxyethyl–Au complexes can be further elaborated in *aqua regia*, notably without cleavage of the two Au–C bonds in the molecule.

Results and Discussion

Synthesis of Au(ppy^H)X_2 (1b–1d for X = Cl, Br, I) and Au(ppy^{Et})X_2 (2b–2d for X = Cl, Br, I)

With $AuCl_3$ (and analogs $HAuCl_4$, $NaAuCl_4$, etc.) readily available, it is not surprising that chloro derivatives dominate much of the Au(III) chemistry. We recently reported the synthesis of the dichloro complexes Au(ppy^H)Cl_2 (**1b**) and Au(ppy^{Et})Cl_2 (**2b**) by a simple synthesis protocol that involved *aqua regia* as the reaction medium.[25] It might be beneficial also to have access to other Au(III) halide congeners. Thus, we first prepared Br and I counterparts of *aqua regia* by mixing 3 volumes of aqueous HBr or HI with 1 volume of HNO_3 to furnish *aqua regia*^{Br} and *aqua regia*^{I}, respectively. Then, it was found that these *aqua regia*$^{Br/I}$ solutions could facilitate substitution of both OAc^F ligands in **1a** and **2a** with Br or I, giving Au(ppy^H)Br_2 (**1c**), Au(ppy^{Et})Br_2 (**2c**), Au(ppy^{Et})I_2 (**1d**), and Au(ppy^{Et})I_2 (**2d**). These reactions proceeded with high product yields and purity, with no further purification required after filtration, washing with water on the filter pad, and drying under air (Scheme 2). Moreover, the reactions did not require prior isolation or purification of the bis(trifluoroacetate) complexes **1a** and **2a**, as the *aqua regia*^{X} treatment could be performed on crude **1a** or **2a** as obtained from the microwave synthesis.[25] The *aqua regia* protocol appears to dissolve metallic or inorganic Au species and impurities, leaving the insoluble **1a–b** and **2a–b** complexes ready to be harvested by filtration. This method circumvents the issues often encountered with other halide exchange methods, such as the presence of side products due to the reduction of Au(III) and tedious purification protocols. We also find that when Au(ppy^R)$(OAc^F)_2$ is treated with HX (X = Cl, Br, I), halide exchange does occur but leads to visually impure materials that are not amenable to efficient purification. The utilization of *aqua regia*^{X} for these transformations is clearly beneficial as it



Scheme 2. Cyclometalation of ppy^H and ppy^{Et} followed by ligand exchange reactions with *aqua regia*$^{Cl/Br/I}$ solutions (prepared with HCl, HBr, or HI) leading to formation of **1b**–**1d** (87, 80, and 79 % yields) and **2b**–**2d** (80, 76, and 63 % yields).

leads to improved yields and purities of products with a simplified work-up procedure.

The products were characterized spectroscopically, by MS, and in some cases by single-crystal X-ray diffraction analysis (vide infra). Some data for **1b** and **2b**, described elsewhere,[25] are included for comparison. By ^{19}F NMR, the absence of signals at δ ca. –76 and –77 in the ^{19}F NMR spectra of the complexes **1a** and **2a** indicated the successful exchange of both trifluoroacetate groups with halides. In the ^{1}H NMR spectra ([D$_6$]DMSO), strong deshielding for the ligand proton α to N of **1b** (δ 10.02), **1c** (δ 10.28), and **1d** (δ 10.49) was seen compared with that in the free *ppy*^{H} diacid ligand (δ 9.17). Furthermore, cyclometalation was also evidenced by the desymmetrization of the ^{1}H NMR pattern (and loss of overall signal intensity corresponding to one H) of the phenyl-ring signals: two signals each of 2H intensity were replaced by three signals of 1H intensity each. Similar features were seen in the ^{1}H NMR spectra of **2b**, **2c**, and **2d** (see ESI for further details).

Electrospray MS in general displayed well-defined molecular ion signals. In particular, the expected isotope distribution patterns were observed in the HRMS spectra of **1c** and **2c** – molecular ions with two ^{79}Br, mixed $^{79/81}$Br, and two ^{81}Br, confirming the presence of two bromide ligands in the complexes. In the HRMS spectra of **1d** and **2d**, only one molecular ion peak was observed.

Aqua Regia Reactions with Au(III) Alkyl Derivatives

We have recently reported how *aqua regia* is beneficial for the high-yield oxidation of various Au(NHC)Cl complexes to Au(NHC)Cl$_3$ congeners, remarkably without cleavage of the Au–C$_{NHC}$ bond under these drastic conditions.[27,28] The new results described above demonstrate how Au(III)–C(sp^2) bonds to (N^C) cyclometalated complexes may also be robust towards protolytic cleavage in *aqua regia*. In the following, we will demonstrate that even Au(III)–C(sp^3) bonds may be similarly robust in *aqua regia*. Interestingly, Roth and Blum have reported that that kinetic basicities of Au(I)–C bonds increase somewhat in the order sp^3 < sp < sp^2.[37]

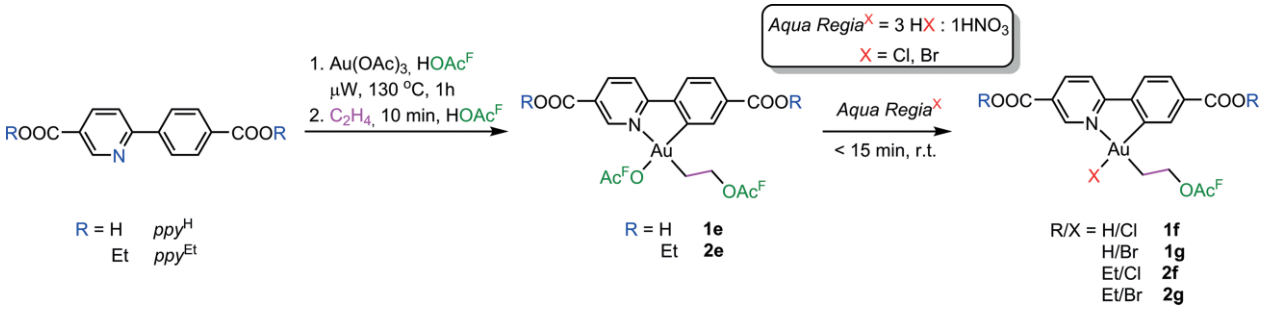
We have reported that ethylene[38] and other alkenes[39] undergo formal insertion into one Au–OAc^F bond in Au(*tpy*)(OAc^F)$_2$ (*tpy* = *p*-tolylpyridine, an N^C chelating ligand; see Scheme 1a) in trifluoroacetic acid. These reactions proceed via an alkene coordination-nucleophilic attack mechanism and occurs selectively at the coordination site *trans* to pyridine-N of the *tpy* ligand. We find that complexes **1a** and **2a** react analogously. When ethylene was bubbled through a warm reaction mixture containing crude **1a** or **2a** in HOAc^F immediately after cyclometalation in the microwave oven, the ethylene insertion products Au(*ppy*^{H})(OAc^F)(CH$_2$CH$_2$OAc^F) (**1e**) and Au(*ppy*^{Et})(OAc^F)(CH$_2$CH$_2$OAc^F) (**2e**) were immediately formed (Scheme 3). These insertions also occurred exclusively *trans* to N. As for the *tpy* system, the insertions were complete in less than 5 min for both the *ppy*^{H} and *ppy*^{Et} complexes. The crude products were obtained by solvent removal under vacuum, and their ^{1}H NMR spectra displayed two characteristic triplets at δ 2.33 and 3.68 (**1e**) and δ 2.32 and 3.66 (**2e**) caused by the two methylene groups derived from inserted ethylene (see ESI for further details). When the crude products **1e** and **2e** were stirred in *aqua regia* for 15 min, substitution of Cl for OAc^F occurred *trans* to C, leading to **1f** and **2f** (Scheme 3), with overall yields of isolated, purified products of 63 % and 71 %, respectively. In the ^{1}H NMR spectra, the triplets of the methylene protons moved significantly to higher ppm values (from 3.68 to 4.73, $\Delta\delta$ = 1.05) and from 2.32 to 2.47, $\Delta\delta$ = 0.15) when **1e** and **2e** converted to **1f** and **2f**. Interestingly, the *aqua regia* treatment caused neither protolytic cleavage of the Au–C(alkyl) bond nor substitution of Cl for OAc^F at the inserted ethylene unit. The presence of trifluoroacetate was confirmed by the presence of sharp singlets at δ = –76.7 and –77.8 (relatively to C$_6$F$_6$) in the ^{19}F NMR spectra of **1f** and **2f**, respectively.

If, however, *aqua regia*^{Br} was used instead of regular *aqua regia*, the Br-substituted species **1g** and **2g** (see Scheme 3) were formed. The diester **2g** was readily isolated in 83 % yield, whereas by contrast the diacid **1g** underwent partial decomposition immediately after the standard workup by filtration and washing with water on a filter. The ^{1}H NMR spectrum of **2g** displays essentially the same features as that of **2f**, the most notable differences being the different downfield change of the resonances arising from the H located α to chelating N and from the Au-bonded methylene group (see ESI for spectroscopic details).

Attempted iodide for OAc^F ligand exchange reacting **1e** and **2e** with *aqua regia*^{I} only resulted in intractable product mixtures.

Crystallographic Structure Determinations of 1c and 1d

X-ray-quality crystals were grown by slow evaporation of solutions of **1c** or **1d** in a dichloromethane/DMSO mixture. Com-



Scheme 3. Cyclometalation followed by reaction with ethylene and ligand exchange reactions.

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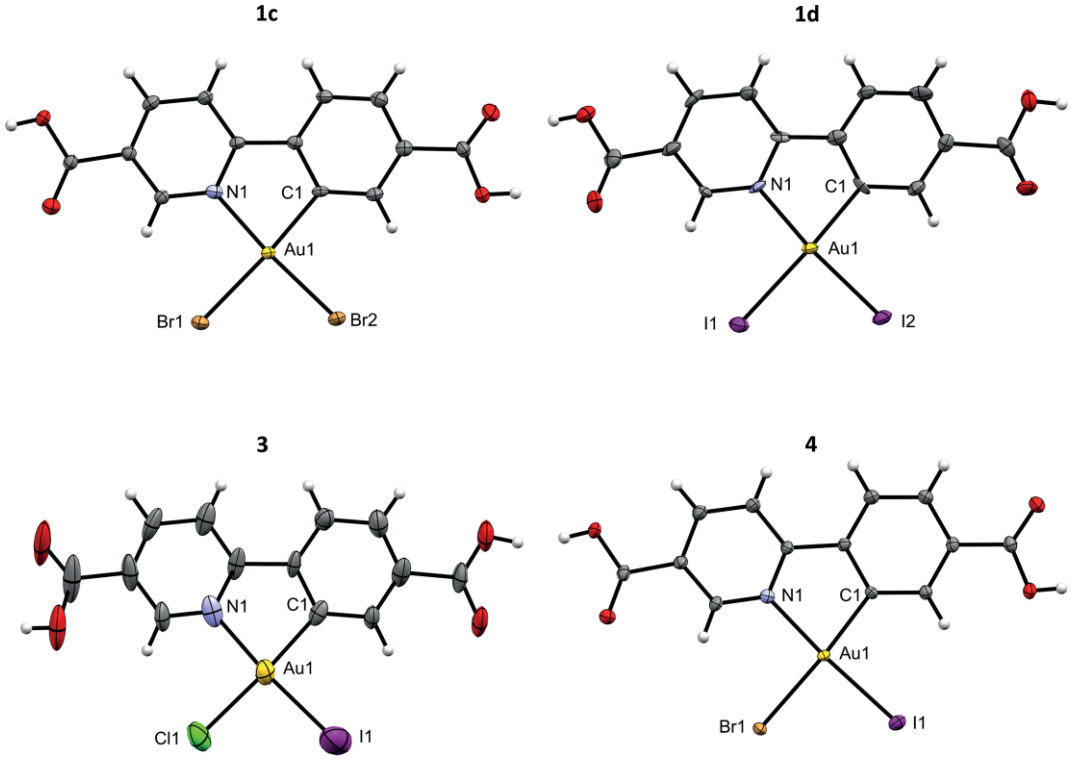

Figure 1. ORTEP plots of the complexes **1c**, **1d**, **3**, and **4**. Thermal ellipsoids are shown at 50 % probability.

plexes **1c** and **1d** form triclinic crystals in the $P\bar{1}$ space group and were found to crystallize with DMSO molecules in the unit cell, associated via hydrogen bonds. ORTEP views of the molecular structures are represented in Figure 1 and selected bond lengths and angles are summarized in Table 1. Data for the previously described structure of the dichloro analogue **1b** are included for the ease of comparison.

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for complexes **1c**, **1d**, **3**, and **4**.

	1c	1d	3[a]	4	1b[b]
Au–N	2.066(3)	2.069(7)	2.08(2)	2.084(3)	2.041(2)
Au–C(1)	2.045(3)	2.05(1)	2.04(2)	2.028(4)	2.025(2)
Au–X(*trans*N)	2.4128(5)	2.5664(8)	2.550(2)	2.5397(4)	2.2713(6)
Au–X(*trans*C)	2.4745(5)	2.6487(9)	2.359(5)	2.5173(5)	2.3613(6)
N-Au–C(1)	81.6(1)	80.0(4)	82.8(6)	80.9(1)	81.63(7)
N-Au–X(*trans*C)	94.31(8)	96.9(2)	93.3(4)	95.09(8)	94.29(5)
C(1)–Au–X(*trans*N)	93.88(9)	94.8(3)	92.5(4)	94.8(1)	93.67(6)
X(*trans*C)–Au–X(*trans*N)	90.20(1)	88.34(3)	91.5(1)	89.24(1)	90.43(2)

[a] See comment in ref.[45] [b] Previously reported and included for comparison, see ref.[25]

The Au(III) complexes **1c** and **1d** display a square-planar coordination geometry as expected for the d^8 electronic configuration. Their carboxylate groups are essentially coplanar with respect to the aromatic rings. Both carboxylic groups in each complex were coordinated via hydrogen bonds with DMSO molecules that were incorporated during the crystallization as solvate molecules. The Au–halogen bond *trans* to C is elongated compared to the one *trans* to N, presumably due to the strong σ-donor and high *trans* influence properties of the phenyl ring. The Au–C distance increases from 2.025(2) Å in the previously reported[25] dichloro complex **1b**, via 2.045(3) Å in the dibromo congener **1c**, to the longest 2.05(1) Å in the diiodo complex **1d**. This trend is in accord with the stronger *trans* influence of iodide and bromide compared to chloride,[40–44] although the steric influences in particular of the two large iodo ligands in **1d** might also contribute. The same trend was observed for the Au–N bond lengths of 2.041(2) Å in **1b**,[25] 2.066(3) Å in **1c**, and 2.069(7) in **1d**. The halide–Au–halide bond angles deviate slightly from the ideal 90°, with values of 90.43(2)° for **1b**, 90.20(1)° for **1c**, and 88.34(3)° for **1d**, respectively.

Halide Metathesis Reactions

The lability of the halide ligands bonded to Au(III) was demonstrated with the formation of the mixed chloro/iodo complex Au(*ppy*^{H})(Cl)(I) (**3**) from a solution of a 1:1 mixture of the dichloro and diiodo complexes **1b** and **1d** in warm (120 °C) [D_6]DMSO. After less than 5 min, the room temperature ^{1}H NMR spectra showed the complete disappearance of the singlet resonances (protons α to N and α to chelate-C) of the reactants **1b** (δ 10.02, 8.32) and **1d** (δ 10.49, and 9.21). The formation of a new complex, identified as the mixed chloro/iodo complex **3** (Scheme 4), was evidenced by the appearance of new resonances at δ 9.97 and 9.61. The ^{1}H NMR spectrum indicated the presence of only one isomer. It was suspected that this might be the one depicted, in which the stronger *trans* influence halide (I) is located *trans* to the weaker *trans* influence donor (pyr-N) of the chelate. This assumption was corroborated by

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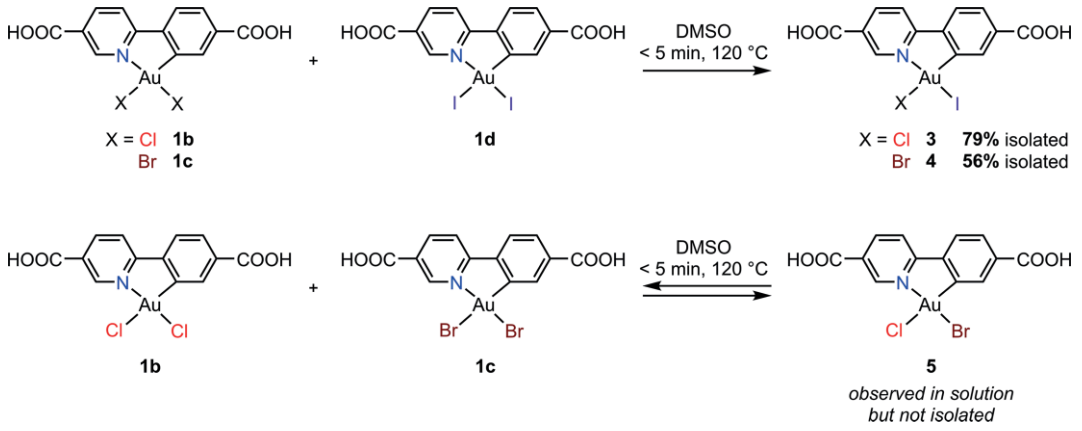

Scheme 4. Halide metathesis reactions between **1b**, **1c**, and **1d** in pairwise combinations.

a molecular structure determination as well as computational studies (vide infra). A preparative-scale reaction led to the isolation of **3** in 79 % yield.

The halide metathesis reaction was not limited to Cl/I exchange but could also applied to Br/I. Thus, the dissolution of **1c** and **1d** in DMSO afforded the mixed bromo/iodo complex **4**, which crystallized in 56 % yield from the reaction mixture during cooling. The aromatic doublets arising from the CH protons at the distal (as seen from Au) side of the chelate appear at essentially the same chemical shifts as in **1c** and **1d**, but the singlets of the protons α to the chelating N or C atoms appeared at altered chemical shifts, from δ 10.49 and 10.28 in **1d** and **1c** to 10.31 in **4** (α-H to chelating N), and from δ 9.21 and 8.69 in **1d** and **1c** to 9.48 in **4** (α to chelating C). Both complexes **3** and **4** were subjected to by single-crystal X-ray diffraction analysis (vide infra).

Finally, completing the combinations of halide metathesis partners, the mixed chloro/bromo complex **5** was observed, albeit only in solution, as suggested through the disappearance of the ^{1}H NMR signals of the reacting dichloro (**1b**) and dibromo (**1c)** partners and concomitant emergence of new signals of **5** in the ^{1}H NMR spectrum (see ESI for details). However, attempts at isolating **5** only resulted in a mixture of the starting materials, **1b** and **1c**, indicating a rapid reversal of the reaction (Scheme 4).

The mixed-halide nature of **3** was verified by high resolution mass-spectroscopy (*m/z* 623.8745 for ^{35}Cl and 625.8718 for ^{37}Cl) with the evidence of one Cl and one I being present together in the molecule. Similarly, *m/z* 643.827 and 645.827 for ^{79}Br and ^{81}Br revealed the presence of one Br and one I in **4**.

Crystallographic Structure Determinations of 3 and 4

Crystals that were suitable for single-crystal X-ray crystallography were obtained by slow cooling to room temperature of a hot solution of **3** in a mixture of CH_2Cl_2 and DMSO. Crystals of **4** were obtained by vapor diffusion of diethyl ether into the reaction mixture of **1c** and **1d** in DMSO. ORTEP views of the molecular structures are shown in Figure 1. Selected bond lengths and angles for the molecular structures of **3** and **4** are listed in Table 1.

The mixed-halide complexes also possess square-planar geometry around the Au(III) center, again with carboxylic groups coplanar with the aromatic rings. The structural studies of **3** and **4** confirm that each complex contains two different halides bonded to the Au center – Cl and I in **3**, and Br and I in **4**. The structure determination also confirms our suspicion that the strongest *trans* influence halide (I > Br > Cl) occupies the coordination site that is *trans* to the weakest *trans* influence end of the chelate (C > N). As expected, this results in significant differences in bond lengths for Au–X(*trans* to N) and Au–X(*trans* to C) for any halide X. Thus, the Au–X(*trans* to C) bond lengths in **3** and **4** (2.359(5) Å and 2.5173(5) Å) are comparable to Au–X(*trans* to C) in **1b** and **1c** (2.3613(6) Å and 2.4745(5) Å) due to the consistent presence of a *trans* phenyl group. Conversely, the Au–I bond lengths in **3** and **4** are slightly shorter than Au–I(*trans* to N) in **1d**, with values of 2.550(2) and 2.5397(4) vs. 2.5664(8) Å, respectively. The chelate angles N-Au–C and X–Au–Y for **3** and **4** fall in the range of those for dihalide complexes **1b-d**.

DFT Calculations on the Relative Thermodynamic Stabilities of Halide Complexes Au(*ppy*^{H})(X)(Y) (1b, 1c, 1d, 3, 4)

In order to shed further light on the experimental findings, in particular on the halide metathesis reactions, a computational study of the halide metathesis reactions was performed using DFT. Scheme 5 depicts the possible set of isodesmic[46–48] reactions in which two different dihalide complexes undergo metathesis to give two identical mixed halide species (in two different coordination geometries). The corresponding Gibbs free energy differences as determined by DFT calculations are also depicted in Scheme 5. As will follow from the discussion below, the outcomes of these reactions are readily rationalized in term of relative trans influences of the halides,[40–44] which dictates their propensities for being located *trans* to C vs. *trans* to N of the chelate.

The reaction between Au(*ppy*^{H})Cl_2 (**1b**) and Au(*ppy*^{H})I_2 (**1d**) led to exclusive formation of Au(*ppy*^{H})(Cl)(I) (**3**), stereoselective with I *trans* to N, a reaction which is substantially more exergonic than formation of its isomer **3′**, where I is positioned *trans*

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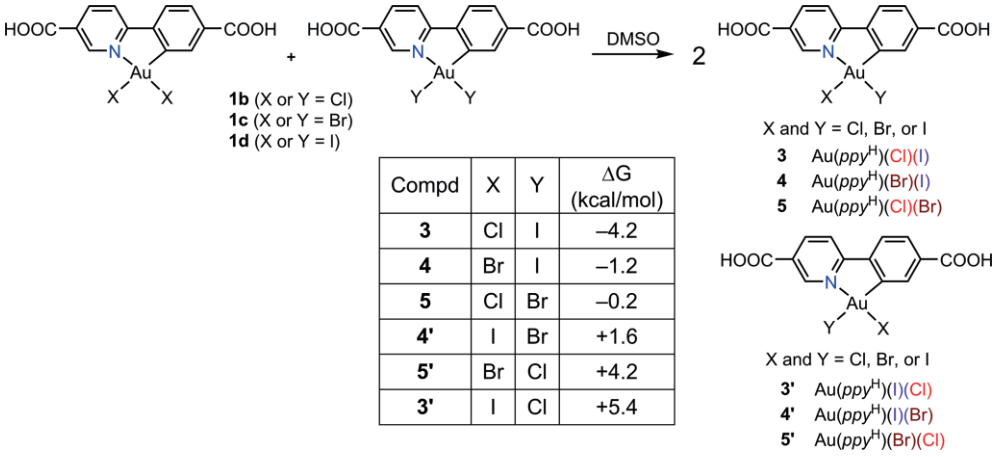

Compd	X	Y	ΔG (kcal/mol)
3	Cl	I	–4.2
4	Br	I	–1.2
5	Cl	Br	–0.2
4'	I	Br	+1.6
5'	Br	Cl	+4.2
3'	I	Cl	+5.4

Scheme 5. Energetics of isodesmic, pairwise halide metathesis reactions of **1b**, **1c**, and **1d** determined by DFT calculations. The numbers indicated are the free energy changes in kcal/mol in DMSO between two of the mixed-halides and the two pertinent starting complexes.

to C (–4.2 vs. +5.4 kcal/mol). Thus, the calculations reveal that positioning I *trans* to N results in a 4.8 kcal/mol more stable complex[49] **3** than its isomer **3′** with I *trans* to C.

Next, the halide metathesis reaction between Au(*ppy*^{H})Br$_2$ (**1c**) and Au(*ppy*^{H})I$_2$ (**1d**) will result in the more favorable complex **4**, with I *trans* to N, rather than its isomer **4′**. The former is preferred by 1.4 kcal/mol, so the energy differences between the Br/I mixed-halide isomers **4** and **4′** are less pronounced than for the Cl/I pair in **5** and **5′**.

The significant differences in energies between the isomers Au(*ppy*^{H})(X)(Y) and Au(*ppy*^{H})(Y)(X) are attributed to the combination of *trans* influence of halides, and of C and N atoms of the chelate ligand – the atom with the highest *trans* influence prefers the atom with lowest *trans* influence located *trans* to itself. This suggests that the observed halide exchange reactions are thermodynamically controlled.

Last, the halide metathesis reaction between dichloro complex **1b** and the dibromo congener **1c** was found to be the least exergonic of the metathesis reactions, with the preferred mixed-halide complex Au(*ppy*^{H})(Cl)(Br) (**5**) being 0.2 kcal/mol Lower in energy than starting **1b** and **1c**. Formation of its isomer, **5′**, with Br *trans* to C, was found to be 4.2 kcal/mol Less favorable than **5**. The rather small energy difference between the reactants and the preferred product indicates an equilibrium constant close to one; almost 30 % of the population will be for **5** at equilibrium. These findings are qualitatively in accordance with experiments. Although the exclusive formation of complex **5** was probably observed in solution by ^{1}H NMR, the attempted isolation of **5** led to reversal to a mixture of the reactants.

Concluding Remarks

A convenient, two-step synthesis of cyclometalated gold(III) phenylpyridine dicarboxylic acids Au(*ppy*^{H})X$_2$ (**1c-d**; X = Br, I) and their diethyl esters Au(*ppy*^{Et})X$_2$ (**2c-d**) have been described. The former should be suitable for installation into UiO-67 type MOFs, as was recently reported for the chloro analogue **1b**. The complexes were prepared reacting bis(trifluoroacetate) complexes **1** and **2** with *aqua regia* solutions containing HBr or HI acids as alternatives to HCl, respectively. The Complexes **1a–b** and **2a–b** exhibit a surprising stability under *aqua regia* conditions, with no protolytic cleavage of Au–C or Au–N bonds to the chelating ligand. The *aqua regia* protocol was extended to the preparation of the cyclometalated gold(III) alkyl-substituted complexes, **1f–g** and **2f–g**, demonstrating that even Au–C(sp^3) bonds are robust under these harsh reaction conditions. These findings may facilitate further exploration of organometallic species in strongly acidic and oxidizing media for synthetic and catalytic applications.

Experimental Section

Computational details

All calculations were carried out at the DFT level with the Gaussian09 program. The hybrid PBE0+D3 GGA functional including Grimme's model for dispersion forces has been used in conjunction with the Stuttgart-Koln basis set including a small-core quasi-relativistic pseudopotential (Au), the LANL08d basis set for the halides (Cl, Br, I) and the all-electron triple-ζ 6-311+G** basis set for the rest of the elements. The ultrafine (99,590) grid was used in the calculation of the integrals for higher numerical accuracy. Geometries were fully optimized without any geometry or symmetry constraint. The solvent effects of DMSO were modeled with the continuum SMD method. Vibrational frequencies were calculated to ascertain that all the optimized structures are true minima on the potential surface. The free energies of the optimized complexes were used to compute the thermochemistry.

Experimental details

General method for preparation of Au(*ppy*^{H})X$_2$ (X = Cl, Br, I for 1b–1d, respectively)

The following procedure is similar to the one recently described by us.[25] A tube for microwave oven synthesis was filled with 6-(4-carboxyphenyl)nicotinic acid (60 mg, 0.248 mmol, 1.0 equiv.), Au(OAc)$_3$ (102 mg, 0.273 mmol, 1.1 equiv.), and trifluoroacetic acid

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(15 mL). The mixture was heated in the microwave oven at 130 °C for 1 h. After cooling to room temperature, the solvent was removed under reduced pressure until dryness. Without purification, the solid (i.e., crude Au(ppy^{H})(OAc^{F})$_2$) was stirred in *aqua regia*^{X} solutions (12 mL) for 30 min. The precipitate was collected on a fine frit filter, washed with water, and dried in air.

Synthesis of Au(ppy^{H})Cl_2 (1b)

The synthesis was carried out according to the general procedure for Au(ppy^{H})X_2 given above. The product was obtained as a pale yellow solid (110 mg, 87 % yield). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 10.02 (d, *J* = 1.9 Hz, 1H; *H5*), 8.78 (dd, *J* = 8.4,1.9 Hz, 1H; *H3*), 8.57 (d, *J* = 8.5 Hz, 1H; *H4*), 8.32 (d, *J* = 1.5 Hz, 1H; *H5′*), 8.15 (d, *J* = 8.1 Hz, 1H; *H4′*), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H; *H3′*). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]DMSO): δ = 165.9 (*C*1′), 165.5 (*C*8), 163.8 (*C*1), 151.1 (*C*2′), 149.1 (*C*H-5), 145.9 (*C*8′), 143.9 (*C*H-3), 133.3 (*C*9), 130.3 (*C*H-5′), 129.9 (*C*H-3′), 128.1 (*C*2), 127.6 (*C*H-4′), 122.9 (*C*H-4). MS (ESI$^+$, CH_3OH) *m/z* (%): 531.939 (100) [^{35} M+Na]$^+$, 533.936 (64) [$^{35/37}$ M+Na]$^+$, 535.933 (11) [^{37} M+Na]$^+$. HRMS (ESI$^+$, CH_3OH) *m/z*: calcd. for $C_{13}H_8Au^{35}Cl_2NNaO_4$: 531.9388, found 531.9386 (+0.5 ppm); also found 533.9357 for $C_{13}H_8Au^{35}Cl^{37}ClNNaO_4$, and 535.9332 for $C_{13}H_8Au^{37}Cl_2NNaO_4$. Anal. calcd. for $C_{13}H_8AuCl_2NO_4$: C, 30.61; H, 1.58; N, 2.75; found C, 30.12; H, 1.63; N, 2.71 %.

Synthesis of Au(ppy^{H})Br_2 (1c)

The synthesis was carried out according to the general procedure for Au(ppy^{H})X_2 given above. The product was obtained as pale orange solid (118 mg, 80 %). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 14.28 (s, 1H; -COO*H*(pyridine)), 13.50 (s, 1H; -COO*H*(Ph)), 10.28 (d, *J* = 1.8 Hz, 1H; *H5*), 8.78 (dd, *J* = 8.4, 1.9 Hz, 1H; *H3*), 8.69 (d, *J* = 1.5 Hz, 1H; *H5′*), 8.58 (d, *J* = 8.5 Hz, 1H; *H4*), 8.18 (d, *J* = 8.2 Hz, 1H; *H4′*), 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H; *H3′*). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]DMSO): δ = 165.9 (*C*1′), 165.6 (*C*8), 163.8 (*C*1), 151.9, 150.1 (*C*H-5), 146.6, 143.6 (*C*H-3), 133.5, 132.3 (*C*H-5′), 129.6 (*C*H-3′), 128.1, 127.8 (*C*H-4′), 123.0 (*C*H-4). MS (ESI$^+$, CH_3OH) *m/z* (%): 619.838 (51) [^{79}M+Na]$^+$, 621.836 (51) [$^{79/81}$ M+Na]$^+$, 623.834 (50) [^{81} M+Na]$^+$, 577.88 [M – COOH+Na]$^+$, 321.971 [H_2L+^{79}Br+H]$^+$, 323.969 [H_2L+^{81}Br+H]$^+$. HRMS (ESI$^+$, CH_3OH) *m/z*: calcd. for $C_{13}H_8Au^{79}BrNNaO_4{}^{81}Br$: 621.8357, found 621.8356 (+0.3 ppm). Anal. calcd. for $C_{13}H_8AuBr_2NO_4$: C, 26.07; H, 1.35; N, 2.34; found C, 26.01; H, 1.37; N, 2.31 %.

Synthesis of Au(ppy^{H})I_2 (1d)

The synthesis was carried out according to the general procedure for Au(ppy^{H})X_2 given above. The precipitate was collected on a fine frit and washed with water and diethyl ether. The product was obtained as dark red solid (137 mg, 79 % yield). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 14.23 (s, 1H; -COO*H*(Py)), 13.45 (s, 1H; -COO*H*(Ph)), 10.49 (d, *J* = 1.8 Hz, 1H; *H5*), 9.21 (d, *J* = 1.5 Hz, 1H; *H5′*), 8.75 (dd, *J* = 8.4, 1.9 Hz, 1H; *H3*), 8.55 (d, *J* = 8.5 Hz, 1H; *H4*), 8.20 (d, *J* = 8.1 Hz, 1H; *H4′*), 8.01 (dd, *J* = 8.0, 1.5 Hz, 1H; *H3′*). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]DMSO): δ = 166.0 (*C*8), 164.0 (*C*1), 153.1, 151.5 (*C*H-5), 148.3, 143.0 (*C*H-3), 136.0 (*C*H-5′), 133.7 (*C*9), 128.8 (*C*H-3′), 128.03 (*C*H-4′), 127.97, 122.9 (*C*H-4). MS (ESI$^-$, CH_3CN): *m/z* 450.776 ([AuI_2^-], 100 %), 691.813 ([M – H$^+$]$^-$, 3 %). MS (ESI$^-$, CH_3OH) *m/z* (%): 691.813 (18) [M – H$^+$]$^-$, 647.824 (<5) [M – H$^+$ – CO_2]$^-$, 595.927 (31) [M – 2H$^+$ – I$^-$+CH_3OH]$^-$. HRMS (ESI$^-$, CH_3OH) *m/z*: calcd. for $C_{13}H_7AuI_2NO_4$: 691.8136, found 691.8132 (+0.5 ppm). Anal. calcd. for $C_{13}H_8AuI_2NO_4$: C, 22.53; H, 1.16; N, 2.02; found C, 21.99; H, 1.19; N, 1.97 %.

General method for synthesis of Au(ppy^{Et})X_2 (X = Cl, Br, I for 2b-d, respectively)

The procedure is analogous to the one recently developed by us.[25] The Teflon liner for microwave oven synthesis was filled with Au(OAc)$_3$ (90 mg, 0.24 mmol, 1.2 equiv.), ethyl 6-(4-(ethoxycarbonyl)phenyl)nicotinate (60 mg, 0.20 mmol, 1.0 equiv.) and trifluoroacetic acid (15 mL). The reaction mixture was heated in the microwave oven at 130 °C for 1 h. After cooling to room temperature, the solvent was removed under reduced pressure until dryness. Without purification, the solid (i.e., crude Au(ppy^{Et})(OAc^{F})$_2$) was stirred in *aqua regia*^{X} solutions (12 mL) for 30 min. The precipitate was collected on a fine frit filter, washed with water, and dried in air.

Synthesis of Au(ppy^{Et})Cl_2 (2b)

The synthesis was carried out according to the general procedure for Au(ppy^{Et})X_2 given above. The product was obtained as a pale yellow solid (90 mg, 80 % yield). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 10.06 (d, *J* = 1.9 Hz, 1H; *H5*), 8.84 (dd, *J* = 8.4, 2.0 Hz, 1H; *H3*), 8.63 (d, *J* = 8.4 Hz, 1H; *H4*), 8.39 (d, *J* = 1.6 Hz, 1H; *H5′*), 8.23 (d, *J* = 8.1 Hz, 1H; *H4′*), 8.04 (dd, *J* = 8.0, 1.6 Hz, 1H; *H3′*), 4.44 (q, *J* = 7.1 Hz, 2H; *H6*), 4.37 (q, *J* = 7.1 Hz, 2H; *H6′*), 1.36 (dt, *J* = 14.3, 7.1 Hz, 6H; *H7* and *7′*). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.41 (d, *J* = 1.8 Hz, 1H; *H5*), 8.78 (dd, *J* = 8.4, 1.8 Hz, 1H; *H3*), 8.67 (d, *J* = 1.4 Hz, 1H; *H5′*), 8.12 (dd, *J* = 8.1, 1.5 Hz, 1H; *H3′*), 8.07 (d, *J* = 8.4 Hz, 1H; *H4*), 7.72 (d, *J* = 8.1 Hz, 1H; *H4′*), 4.52 (q, *J* = 7.1 Hz, 2H; CH_2(6)), 4.44 (q, *J* = 7.1 Hz, 2H; CH_2(6′)), 1.45 (dt, *J* = 19.8, 7.1 Hz, 6H; CH_3(7 and 7′)). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]DMSO): δ = 165.7 (*C*1), 164.4 (*C*1′), 162.3 (C8), 151.0 (C9), 148.8 (*C*H5), 146.2 (C8′), 143.8 (*C*H3), 132.3 (C2′), 129.9 (*C*H5′), 129.8 (*C*H3′), 127.9 (*C*H4′), 127.1 (C2), 123.1 (*C*H4), 62.4 (*C*H$_2$(6)), 61.6 (*C*H$_2$(6′)), 14.14 (*C*H$_3$(7)), 14.06 (*C*H$_3$(7′)). MS (ESI$^+$, CH_3OH) *m/z* (%): 588.002 (7) [*M*+Na$^+$], 584.051 (100), 586.048 (33), 588.002 (19) (*M*+H_3O^+ for *M* with $^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$, respectively). HRMS (ESI$^+$, CH_3OH) *m/z*: calcd. for $C_{17}O_4H_{16}AuN^{35}Cl_2Na$: 588.0014, found 588.0016 (–0.2 ppm); also found 589.9987 for $C_{17}O_4H_{16}AuN^{35}Cl^{37}ClNa$ and 591.9963 for $C_{17}O_4H_{16}AuN^{37}Cl_2Na$. Anal. calcd. for $C_{17}H_{16}AuCl_2NO_4$: C, 36.06; H, 2.85; N, 2.47; found C, 35.78; H, 2.90; N, 2.43 %.

Synthesis of Au(ppy^{Et})Br_2 (2c)

The synthesis was carried out according to the general procedure for Au(ppy^{Et})X_2 given above. The product was washed with water and Et_2O and obtained as pale orange solid (92 mg, 76 %). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 10.30 (d, *J* = 1.9 Hz, 1H; *H5*), 8.82 (dd, *J* = 8.4, 1.9 Hz, 1H; *H3*), 8.71 (d, *J* = 1.5 Hz, 1H; *H5′*), 8.62 (d, *J* = 8.5 Hz, 1H; *H4*), 8.23 (d, *J* = 8.1 Hz, 1H; *H4′*), 8.04 (dd, *J* = 8.1, 1.6 Hz, 1H; *H3′*), 4.44 (q, *J* = 7.1 Hz, 2H; CH_2(6)), 4.37 (q, *J* = 7.1 Hz, 2H; CH_2(6′)), 1.37 (dt, *J* = 15.9, 7.1 Hz, 6H; *H7* and *7′*). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 10.55 (d, *J* = 1.8 Hz, 1H; *H5*), 8.88 (d, *J* = 1.5 Hz, 1H; *H5′*), 8.75 (dd, *J* = 8.4, 1.9 Hz, 1H; *H3*), 8.13–8.06 (m, 2H; *H3′* and *H4*), 7.76 (d, *J* = 8.1 Hz, 1H; *H4′*), 4.50 (q, *J* = 7.1 Hz, 2H; CH_2(6)), 4.41 (q, *J* = 7.1 Hz, 2H; CH_2(6′)), 1.44 (dt, *J* = 23.7, 7.1 Hz, 6H; CH_3(7 and 7′)). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]DMSO): δ = 165.7 (*C*8), 164.4 (*C*1′=O), 162.3 (*C*1), 151.8 (*C*9), 149.9 (*C*H5), 146.9 (C8′), 143.5 (*C*H3), 132.4 (C2′), 132.0 (*C*H5′), 129.5 (*C*H3′), 128.0 (*C*H4′), 127.2 (C2), 123.2 (*C*H4), 62.3 (*C*H$_2$(6)), 61.5 (*C*H$_2$(6′)), 14.1 (*C*H$_3$(7)), 14.0 (*C*H$_3$(7′)). MS (ESI$^+$, CH_3CN) *m/z* (%): 675.900 (8) [^{79} M+Na]$^+$, 677.899 (17) [$^{79/81}$ M+Na]$^+$, 679.897 (8) [^{81} M+Na]$^+$. HRMS (ESI$^+$, CH_3CN) *m/z*: calcd. for $C_{17}O_4H_{16}AuN^{[79/81]}$ Br_2Na: 677.8984, found 677.8985 (–0.2 ppm); also found 675.9004 for $C_{17}O_4H_{16}AuN^{79}Br_2Na$ and 679.8966 for $C_{17}O_4H_{16}AuN^{81}Br_2Na$. Anal. calcd. for $C_{17}H_{16}AuBr_2NO_4$: C, 31.17; H, 2.46; N, 2.14; found C, 31.09; H, 2.41; N, 2.12 %.

Synthesis of Au(ppy^{Et})I_2 (2d)

The synthesis was carried out according to the general procedure for Au(ppy^{Et})X_2 given above. The product was washed with water and acetone to remove iodine. The product was obtained as red solid (95 mg, 63 %). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 10.51 (s, 1H;

H5), 9.23 (s, 1H; *H5′*), 8.80 (d, *J* = 8.5 Hz, 1H; *H3*), 8.58 (d, *J* = 8.4 Hz, 1H; *H4*), 8.25 (d, *J* = 8.1 Hz, 1H; *H3′*), 8.04 (d, *J* = 8.0 Hz, 1H; *H4′*), 4.41 (dq, *J* = 43.2, 7.2 Hz, 4H; -CH_2-(6 and 6′)), 1.37 (dt, *J* = 18.8, 7.2 Hz, 6H; -CH_3(7 and 7′)). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 10.74 (s, 1H; *H5*), 9.35 (s, 1H; *H5′*), 8.72 (dd, *J* = 8.3, 1.9 Hz, 1H; *H3*), 8.11–8.03 (m, 2H; *H3′* and *H4*), 7.79 (d, *J* = 8.1 Hz, 1H; *H4′*), 4.49 (q, *J* = 7.1 Hz, 2H; -CH_2-(6)), 4.40 (q, *J* = 7.1 Hz, 2H; -CH_2-(6′), 1.46 (t, *J* = 7.1 Hz, 3H; -CH_3(7)), 1.42 (t, *J* = 7.1 Hz, 3H; -CH_3(7′). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): δ = 167.5 (*C*8), 165.4 (*C*1′), 163.0 (*C*1), 154.2, 153.1 (*C*H-5), 148.1, 142.9 (*C*H-3), 137.5 (*C*H-5′), 134.6, 129.4 (*C*H-3′), 128.2, 127.1 (*C*H-4′), 122.1 (*C*H-4), 63.3 (-CH_2-(6)), 62.3 (-CH_2-(6′)), 14.6 (-CH_3(7)), 14.5 (-CH_3(7′)). MS (ESI$^+$, CH_3OH) *m/z* (%): 771.873 (12) [M + Na]$^+$, 675.986 (100) [M+$NaOCH_3$]$^+$. HRMS (ESI$^+$, CH_3OH) *m/z*: calcd. for $C_{17}H_{16}AuI_2NO_4Na$: 771.8727, found 771.8727 (–0.0 ppm).

General method for Au(*ppy*^{R})(X)($CH_2CH_2OAc^F$) (X = Cl, Br; R = H, Et for 1f-g and 2f–g)

The Teflon liner for microwave oven synthesis was filled with $Au(OAc)_3$ (68 mg, 0.18 mmol, 1.1 equiv.), *ppy*^{H} or *ppy*^{Et} ligand (0.16 mmol, 1.0 equiv.) and trifluoroacetic acid (15 mL). The reaction mixture was heated in the microwave oven at 130 °C for 1 h. While warm, ethylene gas was bubbled through the reaction mixture for 10 min. The solution was then left to rest for 1 hour. The volatiles were removed under reduced pressure and afforded Au(*ppy*^{R})(OAc^F)($CH_2CH_2OAc^F$) (**1a**, **2a**) as pale-yellow solids. Without purification, the solid was stirred in *aqua regia*^{X} solutions (12 mL) for 15 min. The precipitate was collected on a fine frit filter, washed with water, and dried in air.

Synthesis of Au(*ppy*^{Et})(Cl)($CH_2CH_2OAc^F$) (2f)

The synthesis was carried out according to the general procedure for Au(*ppy*^{R})(X)($CH_2CH_2OAc^F$) given above. The product was obtained as a pale yellow solid (76 mg, 71 % yield). ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 9.56 (d, *J* = 2.0 Hz, 1H; *H5*), 8.64 (dd, *J* = 8.4, 2.1 Hz, 1H; *H3*), 8.50 (d, *J* = 8.5 Hz, 1H; *H4*), 8.21 (d, *J* = 8.2 Hz, 1H; *H4′*), 7.97 (s, 1H; *H5′*), 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H; *H3′*), 4.69 (t, *J* = 7.8 Hz, 2H; Au-CH_2-CH_2-), 4.41 (q, *J* = 7.1 Hz, 2H; *H6*), 4.34 (q, *J* = 7.1 Hz, 2H; *H6′*), 2.47 (m, 2H; Au-CH_2-CH_2-), 1.37 (dt, *J* = 10.3, 7.1 Hz, 6H; *H7* and *H7′*). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 9.94 (d, *J* = 1.7 Hz, 1H; *H5*), 8.66 (dd, *J* = 8.4, 2.0 Hz, 1H; *H3*), 8.29 (d, *J* = 1.5 Hz, 1H; *H5′*), 8.13 (d, *J* = 8.3 Hz, 1H; *H4*), 8.09 (dd, *J* = 8.1, 1.5 Hz, 1H; *H3′*), 7.95 (d, *J* = 8.2 Hz, 1H; *H4′*), 4.83–4.77 (m, 2H; -CH_2-OAc^F), 4.48 (q, *J* = 7.1 Hz, 2H; CH_2(6)), 4.41 (q, *J* = 7.1 Hz, 2H; CH_2(6′)), 2.78–2.71 (m, 2H; Au-CH_2-), 1.43 (dt, *J* = 17.4, 7.1 Hz, 6H; *H7* and *H7′*). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): δ = 165.8, 163.9, 163.6, 157.7 (q, *C*O, *J* = 40.8 Hz), 149.5, 147.1, 146.4, 142.6 (*C*H3), 134.2, 131.2 (*C*H5′), 129.6 (*C*H3′), 128.2, 126.7 (*C*H4′), 120.8 (*C*H4), 114.9 (q, *C*F3, *J* = 286.9 Hz), 68.89 (-CH_2-OAc^F), 62.9 (-CH_3(7)), 62.1 (-CH_2(6)), 27.2 (Au-CH_2-), 14.4 (-CH_3(7′)), 14.3 (-CH_2(6′)). ^{19}F NMR (400 MHz, CD_2Cl_2): δ = –77.8 (s, -OCOCF_3), –164.9 (s, C_6F_6, internal standard). MS (ESI$^+$, CH_3CN) *m/z* (%): 694.049 (100) [*M* + Na]$^+$, 598.067 (70) [*M* – COOEt]$^+$. HRMS (ESI$^+$, CH_3CN) *m/z*: calcd. for $C_{21}H_{20}AuClF_3NO_6$: 694.0489, found 694.0491 (–0.3 ppm). Anal. calcd. for $C_{21}H_{20}AuClF_3NO_6$: C, 37.55; H, 3.00; N, 2.08; found C, 36.15; H, 2.91; N, 1.99 %.

Synthesis of Au(*ppy*^{Et})(Br)($CH_2CH_2OAc^F$) (2g)

The synthesis was carried out according to the general procedure for Au(*ppy*^{R})(X)($CH_2CH_2OAc^F$) with slight modifications. After bubbling of the ethylene gas, the solution was left at room temperature for 2 hours before the solvent was removed under reduced pressure. The crude solid was immediately stirred with a fresh mixture of HBr (9 mL) and HNO_3 (3 mL) for 5 min. Dilution with water followed by filtration afforded product as a pale orange solid (97 mg, 83 %). ^{1}H NMR (600 MHz, [D_6]DMSO): δ = 9.80 (s, 1H; *H5*), 8.63 (dq, *J* = 8.4, 2.0, 1.6 Hz, 1H; *H3*), 8.51 (dd, *J* = 8.6, 2.7 Hz, 1H; *H4*), 8.23–8.18 (m, 1H; *H4′*), 7.95 (s, 1H; *H5′*), 7.94–7.90 (m, 1H; *H3′*), 4.69 (t, *J* = 8.0 Hz, 2H; Au-CH_2-CH_2-), 4.41 (q, *J* = 7.1 Hz, 2H; *H6*), 4.34 (q, *J* = 7.1 Hz, 2H; *H6′*), 2.59 (t, *J* = 7.2 Hz, 2H; Au-CH_2-CH_2-), 1.37 (dt, *J* = 14.5, 7.1 Hz, 6H; *H7* and *H7′*). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 10.18 (d, *J* = 2.1 Hz, 1H; *H5*), 8.64 (dd, *J* = 8.4, 2.1 Hz, 1H; *H3*), 8.26 (d, *J* = 1.6 Hz, 1H; *H5′*), 8.16–8.07 (m, 2H; *H4* and *H3′*), 7.94 (d, *J* = 8.1 Hz, 1H; *H4′*), 4.80 (t, *J* = 8.0 Hz, 2H; -CH_2-OAc^F), 4.47 (q, *J* = 7.2 Hz, 2H; *H6*), 4.41 (q, *J* = 7.1 Hz, 2H; *H6′*), 2.91–2.80 (m, 2H; Au-CH_2-), 1.51–1.34 (m, 6H; *H7* and *H7′*). ^{13}C{^{1}H} NMR (151 MHz, [D_6]DMSO): δ = 164.8, 162.9, 162.6, 156.2 (q, *C*O, *J* = 40.6 Hz), 149.3, 147.2, 146.9, 142.3, 132.5, 128.9, 128.9, 127.6, 127.3, 122.1, 114.1 (q, *C*F_3, *J* = 286.2 Hz), 68.6, 62.0, 61.3, 25.4, 14.0, 13.9. ^{19}F NMR (400 MHz, CD_2Cl_2): δ = -77.7 (s, -OCOCF_3), –164.9 (s, C_6F_6, internal standard). MS (ESI$^+$, CH_3CN) *m/z* (%): 636.090 (100) [*M* – Br]$^+$. HRMS (ESI$^+$, CH_3CN) *m/z*: calcd. for $C_{21}H_{20}AuF_3NO_6$ [M – Br]$^+$: 636.0903, found 636.0902 (+0.2 ppm). Anal. calcd. for $C_{21}H_{20}AuBrF_3NO_6$: C, 35.22; H, 2.81; N, 1.96; found C, 35.24; H, 2.79; N, 1.96 %.

Synthesis of Au(*ppy*^{H})(Cl)($CH_2CH_2OAc^F$) (1f)

The synthesis was carried out according to the general procedure for Au(*ppy*^{R})(X)($CH_2CH_2OAc^F$) given above. The product was obtained as a pale yellow solid (62 mg, 63 % yield). ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 9.70 (s, 1H; *H5*), 8.68 (d, *J* = 8.4 Hz, 1H; *H3*), 8.57 (d, *J* = 8.5 Hz, 1H; *H4*), 8.29 (d, *J* = 8.2 Hz, 1H; *H4′*), 8.09 (s, 1H; *H5′*), 7.99 (d, *J* = 7.9 Hz, 1H; *H3′*), 4.73 (t, *J* = 7.6 Hz, 2H; Au-CH_2-CH_2-), 2.57 (t, *J* = 7.6 Hz, 2H; Au-CH_2-CH_2-). ^{13}C{^{1}H}NMR (151 MHz, [D_6]DMSO): δ = 166.5 (*C*1′), 164.5 (*C*8), 162.5 (*C*1), 156.2 (q, *C*O, *J* = 40.8 Hz), 148.1 (*C*2′), 146.9 (*C*5), 145.1 (*C*8′), 142.7 (*C*3), 133.5 (*C*9), 129.9 (*C*5′), 129.1 (*C*3′), 128.0 (*C*2), 127.4 (*C*4′), 121.74 (*C*4), 114.0 (q, *C*F3, *J* = 286.9 Hz), 68.67 (-CH_2-OAc^F), 26.29 (Au-CH_2-CH_2-). ^{19}F NMR (400 MHz, [D_6]DMSO): δ = –76.6 (s, -OCOCF_3), –164.9 (s, C_6F_6, internal standard). MS (ESI$^-$, CH_3CN) *m/z* (%): 613.990 (100) [M – H]$^-$, 570.000 (11) [*M* – COOH]$^-$. HRMS (CH_3CN) *m/z*: 613.9901 (calculated for [$C_{17}H_{11}AuClF_3NO_6$]$^-$ 613.9898 (–0.4 ppm)). Anal. calcd. for $C_{17}H_{12}AuClF_3NO_6$: C, 33.16; H, 1.96; N, 2.27; found C, 32.81; H, 2.06; N, 2.25 %.

General method for synthesis of Au(*ppy*^{H})(X)(Y) – metathesis reaction

A mixture of Au(*ppy*^{H})X_2 (0.036 mmol) and Au(*ppy*^{H})Y_2 (0.036 mmol) was dissolved under while heating to 120 °C and stirring in DMSO (1.4 mL). The resulting clear solution was left to cool down to ambient temperature. The formed precipitate was filtered, washed with CH_2Cl_2 and dried under a flow of air to yield the complex Au(*ppy*^{H})(X)(Y).

Au(*ppy*^{H})(Cl)(I) (3)

Intensive orange solid. Yield 79 % (17 mg). ^{1}H NMR (600 MHz, [D_7]DMF): δ = 9.97 (s, 1H; *H5*), 9.61 (s, 1H; *H5′*), 8.93 (dd, *J* = 8.3, 1.9 Hz, 1H; *H3*), 8.69 (d, *J* = 8.3 Hz, 1H; *H4*), 8.35 (d, *J* = 8.0 Hz, 1H; *H4′*), 8.12 (dd, *J* = 8.0, 1.5 Hz, 1H; *H3′*). ^{1}H NMR (600 MHz, [D_6]DMSO): δ = 9.75 (s, 1H; *H5*), 9.42 (s, 1H; *H5′*), 8.79 (dd, *J* = 8.4, 1.9 Hz, 1H; *H3*), 8.54 (d, *J* = 8.4 Hz, 1H; *H4*), 8.24 (d, *J* = 8.1 Hz, 1H; *H4′*), 8.01 (dd, *J* = 8.1, 1.5 Hz, 1H; *H3′*). ^{13}C{^{1}H} NMR (151 MHz, [D_6]DMSO): δ = 165.8 (*C*1′), 165.4 (*C*8), 164.1 (*C*1), 148.2, 147.5, 146.1 (*C*5), 143.7 (*C*3), 139.4 (*C*5′), 134.4, 128.9 (*C*3′), 127.9 (*C*4′), 127.2, 122.6 (*C*4). MS (ESI$^+$, CH_3OH) *m/z* (%): 623.875 (26) [M + Na]$^+$, 565.916 (6) [M – Cl]$^+$. HRMS (ESI$^+$, CH_3OH) *m/z*: calcd. for $C_{13}H_8Au^{35}ClINO_4Na$: 623.8750, found 623.8744 (–0.1 ppm); found also *m/z* 625.8718 for $C_{13}H_8Au^{37}ClINO_4Na^+$.

Au(*ppy*^{H})(Br)(I) (4)

Orange-red solid. Yield 56 % (13 mg). ^{1}H NMR (400 MHz, [D$_7$]DMF): δ = 10.31 (s, 1H; *H5*), 9.48 (s, 1H; *H5'*), 8.92 (dd, *J* = 8.4, 1.9 Hz, 1H; *H3*), 8.70 (d, *J* = 8.5 Hz, 1H; *H4*), 8.35 (d, *J* = 8.2 Hz, 1H; *H4'*), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H; *H3'*). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 14.24 (s, 1H; -COO*H*(pyr)), 13.46 (s, 1H; -COO*H*(Ph)), 10.07 (s, 1H; *H5*), 8.77 (dd, *J* = 8.3, 1.8 Hz, 1H; *H3*), 8.54 (d, *J* = 8.4 Hz, 1H; *H4*), 8.22 (d, *J* = 8.1 Hz, 1H; *H4'*), 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H; *H3'*). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]DMSO): δ = 165.8, 165.6, 164.0, 150.5, 148.1 (*C*5), 147.6, 143.4 (*C*3), 134.1, 129.0 (*C*3'), 128.0 (*C*4'), 127.6, 122.8 (*C*4). MS (ESI$^-$, CH_3OH) *m/z* (%): 643.827 [^{79} M – H]$^-$, 645.825 [^{81} M – H]$^-$. MS (ESI$^+$, CH_3OH) *m/z* (%): 623.834 (50) [^{81} M+Na]$^+$, 577.88 [M – COOH+Na]$^+$, 321.971 [H_2L+^{79}Br+H]$^+$, 323.969 [H_2L+^{81}Br+H]$^+$. MS (ESI$^-$, CH_3CN) *m/z* (%): 643.827 (53) and 645.825 (49) [*M* – H]$^-$, 599.837 (31) and 601.835 [*M* – COOH]$^-$. HRMS (ESI$^-$, CH_3CN) *m/z*: calcd. for $C_{13}H_7Au^{79}BrINO_4$: 643.8274, found 643.8271 (+0.5 ppm); found also *m/z* 645.8251 for $C_{13}H_7Au^{81}BrINO_4$. Anal. calcd. for $C_{13}H_8AuClINO_4$: C, 25.96; H, 1.34; N, 2.33; found C, 25.23; H, 1.44; N, 2.24 %.

Deposition Numbers 1972234 (for **1c**), 1972233 (for **1d**), 1972232 (for **3**), and 1972235 (for **4**) 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.

Supporting information (see footnote on the first page of this article): Experimental procedures, spectroscopic and crystallographic data.

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