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Catalytic studies of cyclometalated gold(III) complexes and their related UiO-67 MOF



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ABSTRACT

Cyclometalated gold(III) complexes Au(L)(OAc^F)₂ (L = phenylpyridine dicarboxylic diester (ppyde) or phenylpyridine dicarboxylic acid (ppydc)) have been prepared reacting Au(OAc)₃ with corresponding phenyl pyridines (ppyde or ppydc) in trifluoroacetic acid (HOAc^F) under microwave heating. Further treatment of Au(L) (OAc^F)₂ with *aqua regia* resulted in dichloro complexes Au(L)Cl₂. Au-functionalized UiO-67 MOF has been synthesized by exchanging linkers of UiO-67 with Au(ppydc)Cl₂, furnishing the MOF with (N[°]C)-cyclometalated Au(III) centers. The catalytic activities of the molecular cyclometalated complexes and the Au-incorporated MOF were studied in gold-catalyzed propargyl ester cyclopropanations. Almost all complexes and the MOF showed catalytic activity to the cyclopropanation product (up to 97% conversion), with a preference for the *trans* diastereoisomer (up to 14:86 d.r.). The recyclability of the most active molecular complex has also been investigated.

1. Introduction

Gold catalysis comprises one of the most effective methods for the activation of C-C double and triple bonds leading to broad diversity of follow-up chemical transformations, such as heterocycles and natural compounds syntheses [1-5]. In the field of gold catalysis, the development of Au(I) catalysts has dominated over Au(III) catalysts, due to the superior stability of Au(I) salts compared to Au(III) salts. However, stable Au(III)-ligated complexes have been developed and studied for their bioactivity, such as anticancer and inhibition of DNA/RNA synthesis [6,7]. Au(III) complexes that have been used in catalysis have been primarily less robust and ligand-free Au(III) species, with some exceptions such as pincer (C^C^N)Au and (C^C)Au complexes [8-12]. In the past decade, Au(III) complexes as catalysts have gained popularity due, in part, to the development of robust synthetic procedures [13]. The Tilset group has reported the syntheses of various cyclometalated Au(III) complexes using microwave heating [14-16]. (N^C)Au complexes bearing a phenyl pyridine ligand (ppy) are extensively studied complexes with various substituents on aromatic rings. This class of cyclometalated complexes has proven to be active in the catalysis of a large range of reactions, including aromatic addition to vinyl ketones [17], AAA-coupling reaction [18,19] and oxazole synthesis [20].

The ppy motif, as a ligand in cyclometalated metal complexes, has potential uses in the MOF community, especially in heterogeneous catalysis [21]. One family of MOFs that has attracted widespread attention is the UiO-series – UiO-66, UiO-67 and UiO-68 [22]. Due to their high thermal and chemical stability and ease of modification, they have been utilized for incorporation of various metal-functionalized linkers. However, the incorporation of the ppy ligand into UiO-67 is yet to be explored with gold, although reports with Ir, Ru and Rh exist (Fig. 1) [21,23–25].

The introduction of a gold linker with a covalent Au–C bond is expected to increase the robustness and recyclability of the catalytic material and give better catalytic performance. Existing reports on covalently-bonded Au-MOFs are limited. While this work was in preparation, Toste and co-workers reported a stabilization of (C^C)Au(III) complexes by inclusion into MOFs [26]. The catalytic results indicated an enhanced stability of the supported Au complex compared to its molecular analogue. The attempted inclusion of (salen)–Au(III) complex into a IRMOF-3 framework has been reported, but was discovered to contain mostly Au(0) species [27]. Later, a proline-functionalized IRMOF-3 with Au active centers was reported, but analysis revealed inclusion of both Au(III) and Au(0) species [28]. Other than one Schiff base Au(III)-functionalized IRMOF-3 and the recent work by Toste

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Fig. 1. Reported cyclometalated metal complexes, from left to right: Linker for the UiO-67 MOF, cyclometalated iridium complexes [23,25], cyclometalated ruthenium complexes [24] and cyclometalated gold complexes described in this work.

[26,29], no other stable covalently-bonded Au(III) complexes have been incorporated into a MOF. The goal of this investigation was to incorporate the Au(ppydc) unit into the UiO-67 MOF framework and study the catalytic activity of the Au(III)-MOF in a gold-catalyzed reaction. The Au(ppydc) unit contains a stable Au-metallacycle comprised of covalent Au–C and coordinative Au–N bonds and is expected to give a robust, heterogeneous catalyst, capable of carrying out a range of gold-catalyzed reactions [30].

This work demonstrates the successful incorporation of an Au(III)functionalized linker into the framework of the UiO-67 MOF. The resulting MOF was tested in a cyclopropanation reaction and compared to its molecular cyclometalated Au(III) analogs in solution.

2. Results and discussion

2.1. Synthesis and characterization of cyclometalated Au(III) complexes

The cyclometalation of ppydc and ppyde with $Au(OAc)_3$ in $HOAc^F$ under microwave heating resulted in formation of complexes **1a** and **1b** in 46% and 65% yields, respectively (Scheme 1).

The ¹H NMR spectra of the complexes **1a** and **1b** were compared to those of uncomplexed ligands ppydc and ppyde and revealed one proton less in the cyclometalated complexes. The loss of a proton at the chelating C and appearance of a singlet to its neighbor H at δ 7.50 and 7.51 in the ¹H NMR spectra of **1a** and **1b**, respectively, indicated the formation of the Au–C covalent bond. Also, the ¹⁹F NMR spectrum revealed two signals corresponding to OAc^F groups.

Initial attempts to substitute OAc^F groups by Cl in treatment with aqueous NaCl or HCl resulted in full exchange of OAc^F groups and led to formation of **2a** and **2b**. The reaction was followed by ¹⁹F NMR spectroscopy and the disappearance of the two fluorine signals confirmed complete Cl-ion exchange. One major drawback of this method of preparation is that the reaction results in **2b** and **2a** which appears as a grey material presumably due to contamination with NMR-silent inorganic gold species. The inorganic gold species can be removed by washing **1a** with *aqua regia*, in a protocol that was previously employed in our group [**31**,**32**]. In addition to the dissolution of inorganic Au species, *aqua regia* substituted OAc^F groups with Cl, furnishing pure **2a** and **2b** in 87% and 80% yields, respectively, after two steps.

The absence of signals in the ^{19}F NMR spectra of the complexes **2a** and **2b** indicated the successful exchange of the OAc^F groups with halides. A strong deshielding for the proton α to the chelating N in the ^{1}H

NMR spectrum of **2a** (δ 10.02) and **2b** (δ 10.06) compared with that of the free ppydc and ppyde ligands (δ 9.18 in both ligands) indicated a successful cyclometalation. A similar deshielding effect was observed for protons α to chelating C atom in **2a** (δ 8.33) and **2b** (δ 8.39) compared to those in ppydc (δ 8.27) and ppyde (δ 8.29) (see ESI). The molecular ions with expected isotope distribution were observed in the high-resolution mass-spectra of the complexes – two ³⁵Cl, one ^{35/37}Cl and two ³⁷Cl ions for **2a,b** confirming the presence of two halogen atoms in the complex (see ESI).

Crystals suitable for structure determination by X-ray diffraction analysis were obtained by vapor diffusion of dichloromethane into the trifluoroacetic acid solution for **1a**, pentane into dichloromethane solution for **1b** and dichloromethane into DMSO solution for **2a**. The ORTEP figures and the selected bond distances as well as angles are summarized and depicted in Fig. 2.

The solid-state structures of **1a** and **1b** reveal the expected squareplanar geometry around the Au(III)-center. In both complexes the Au–O bond which is *trans* to carbon atom is elongated compared to the one *trans* to nitrogen due to the stronger *trans* influence of aryl-C *vs* pyr-N (2.064(3) *vs* 2.047(3) Å in **1b** and 2.088(3) *vs* 2.006(2) Å in **1a**). The Au–C distances are similar, 1.993(3) and 1.991(3) Å in **1b** and **1a** respectively. The bond angles around the central Au atom are also similar in **1a** and **1b** with no differences greater than 3° for both complexes. The carbonyl groups in **1a** and **1b** were found to be planar with respect to aromatic system. The Au–Cl bond distances in **2a** of 2.2713(6) (*trans* to N) and 2.3613(6) (*trans* to C) Å are typical for (N°C)AuCl₂ complexes, which span the range 2.262–2.282 Å for *trans* to N and 2.361–2.372 Å for *trans* to C. [33–35]

2.2. Synthesis and characterization of MOF

Our initial attempts to synthesize a Au(III)-functionalized UiO-67 MOF focused on direct assembly from the starting building blocks (ZrCl₄, H₂bpdc and complex **1a** or **2a**) in DMF at 120 °C in the presence of benzoic acid as a modulator. Despite the success of the direct assembly for other metal-functionalized MOFs [25], this synthesis method resulted in UiO-67 with no incorporation of Au as evidenced by single-crystal X-ray diffraction analysis. The absence of Au in the isolated material may be attributed to the reduction of Au(III) with amines that were generated during the synthesis. Such reduction during the synthesis was also observed for other types of Au-functionalized MOFs [27].



Scheme 1. Synthesis of complexes 1a and 1b followed by ligand exchange in aqua regia furnishing complexes 2a and 2b.

V.A. Levchenko, et al.



Fig. 2. ORTEP representation of crystal structures of **1a**, **b** and **2a** with atoms drawn using 50% probability ellipsoids. Selected bond distances (Å) and angles (deg), for **1a**: Au1-N1 2.008(2), Au1-C1 1.991(3), Au1-O3 2.006(2), Au1-O1 2.088(3), N1-Au1-C1 81.9(1), C1-Au1-O3 93.7(1), O3-Au1-O1 92.51(9), O1-Au1-N1 91.8(1). For **1b**: Au1-N1 2.002(3), Au1-C7 1.993(3), Au1-O1 2.064(3), Au1-O3 2.047(3); N1-Au1-C7 81.7(1), C7-Au1-O3 94.8(1), O3-Au1-O1 88.5(1), O1-Au1-N1 95.0(1). For **2a**: Au1-N1 2.041(2), Au1-C1 2.025(2), Au1-C1 2.3613(6), Au1-C12 2.2713(6); N1-Au1-C1 81.63(7), C1-Au1-C12 93.67(6), Cl2-Au1-Cl1 90.43(2), Cl1-Au1-N1 94.29(5).

The destructive reduction of the Au-linker has been overcome by employing a post-synthetic linker exchange (PSLE) [36] protocol to substitute the biphenyl linker in UiO-67 with a gold(III) ppydc unit (Scheme 3). The PSLE was carried out by heating UiO-67 with 1a or 2a in DMSO at 85 °C in the microwave oven for 6 h. This method was successful for complex 2a to give MOF UiO-67-[Au]Cl, but 1a was thermally unstable under these conditions and incorporation of 1a into the MOF failed.

The obtained UiO-67-[Au]Cl was isolated as a pale-yellow powder, after washing with hot DMSO and acetone followed by activation under dynamic vacuum. The crystallinity of UiO-67 was retained after incorporation of 2a, as evidenced by powder X-ray diffraction analysis and SEM (Figs. 3a and c). Energy-dispersed X-ray spectroscopy (EDS) was used to study the spatial distribution of gold in MOF. EDS elements mapping on UiO-67-[Au]Cl showed a homogeneous distribution of Au within the MOF (Fig. 3f). Activated UiO-67-[Au]Cl exhibited a Braunauer-Emmett-Teller (BET) surface area of $867 \text{ m}^2/\text{g}$, which is less than half the BET of the original UiO-67 ($2113 \text{ m}^2/\text{g}$), and their nitrogen absorption isotherms are depicted in Fig. 3d. The decrease in surface area can be attributed to the smaller pore size due to the presence of the Au-functionalized linkers in the pores. The Au-functionalization had surprisingly a little impact on MOF's thermal stability, which is stable up to 400 °C and is comparable to the unfunctionalized UiO-67 MOF (Fig. 3b), according to TGA measurements.

The presence of the Au(ppy) units in UiO-67-[Au]Cl was confirmed by ¹H NMR spectroscopy of the digested material in 1 M D₃PO₄ in DMSO- d_6 . The degree of functionalization was calculated by integration of the proton resonances for bpdc and ppydc in ¹H NMR spectrum, which showed 16% Au-substitution. This corresponds to the replacement of one out of six bpdc linkers with a Au linker (see ESI for calculations). Linker exchange in single crystals of UiO-67 was carried out under the same conditions used for the bulk samples. Single crystal Xray structure determination of UiO-67-[Au]Cl showed a successful incorporation of the Au(ppydc) unit into the UiO-67 framework (Fig. 4). One of the linkers shows thermal vibrations of the aryl groups of the linker, and the position and thermal vibrations of the partially occupied Au atom. The occupancy of the Au atom is slightly below 1%, and it is disordered by symmetry over four equivalent sites. Other ligands of the Au atom are missing from the structure due to disorder and their poor scattering power.

2.3. Catalytic studies of gold complexes

The catalytic activity of diacids **1a** and **2a**, diesters **1b** and **2b**, and UiO-67-[Au]Cl was studied in the cyclopropanation reaction between propargyl ester **3** and styrene (**4**) [37] in DCM at room temperature using 10 mol% of gold catalyst (Scheme 2b). The reaction progress was monitored by ¹H NMR spectroscopy (Fig. 5 and Table 1). The previously published NMR study of this reaction with butyl-bisoxazoline-Au(III) (BOX) complexes showed high activity with gold(III) complexes and an interesting *cis-trans* isomerization (Scheme 2c) [37].

Complexes **1b**, **2a** and **2b** showed catalytic activity over 24 h (45–97% conversion, Fig. 5 and Table 1, entries 2–4) with **2b** as the most efficient catalyst (conversion > 95% after 4 h), giving quantitative yield after isolation (Fig. 5 and Table 1, entry 4). Changing the solvent from CH_2Cl_2 to DMSO- d_6 or MeCN- d_3 completely retarded the catalytic activity of **2b**.

The bis(trifluoroacetate) analogue **1b** resulted in lower conversion (77%, 24 h, Table 1, entry 3), which is presumably due to the decomposition of the catalyst. After only 4 h, a deep purple color had evolved, indicating the possible reduction of the catalyst to gold nanoparticles. Examination of the ¹H NMR data also revealed a reduction in the concentration of complex **1b**. In comparison, complex **2b** remained stable through the whole catalytic run, with no signs of degradation.

Generally, the complexes 1b and 2b are much more active than 1a and 2a (Fig. 5 and Table 1, entries 3 and 4 vs 1 and 2), where the differences appeared to correspond to catalyst solubility in DCM- d_2 (soluble 1 - 2b and insoluble 1 - 2a). Despite the insolubility of 2a, the complex showed moderate activity (45% conversion, 24 h, Table 1, entry 2). The catalytic nature of the apparently insoluble 2a was investigated by stirring 2a in DCM-d₂ for 24 h, filtering off the solids and mixing the filtrate with the propargyl ester 3 and styrene (4). NMR analysis of the mixture over 24 h showed no conversion, indicating that catalysis occurs in a heterogeneous manner for complex 2a. An additional experiment was performed by stirring 2a with propargyl acetate 3 and styrene (4) for 1 h followed by filtration of the suspension and subjecting the solute to the ¹H NMR. Absence of conversion of propargyl acetate 3 supported the heterogeneous nature of the catalysis. The reactions were conducted several times and, in all cases, catalytic activity was observed, although results appeared to be sensitive to the quality of the substrate, styrene or catalyst.

Recent literature on the catalytic activity of cationic BOX-Au(III)



Fig. 3. (a) PXRD patterns of UiO-67 and UiO-67-[Au]Cl. (b) TGA plots of UiO-67 and UiO-67-[Au]Cl. (c) SEM image of UiO-67-[Au]Cl. (d) Nitrogen sorption isotherm of UiO-67-[Au]Cl. (e) ¹H NMR (400 MHz, DMSO-d₆) spectra of 2a and UiO-67-[Au]Cl. (f) Au mapping of UiO-67-[Au]Cl by EDX.



Fig. 4. Structure of UiO-67[Au]Cl showing a partial unit cell.

complexes and neutral Au(III) complexes (AuCl₃ and pyr-menthone-AuCl₂) report that cationic Au(III) complexes show higher catalytic activity than the neutral complexes (Scheme 2c) [37]. Ligand exchange of complex **2b** was therefore attempted with AgOTf, NaPF₆ and NaBAr^F prior to mixture with the reagents.

The cyclopropanation reaction catalyzed by complex **2b**/AgOTf resulted in immediate formation of Au nanoparticles, but also full conversion within the first few minutes of the reaction with no further changes over the next 24 h (Table 1, entry 5). Reactions using **2b**/NaPF₆ or NaBAr^F resulted in immediate decomposition of the gold complex and/or propargyl ester **3** to unknown products (Table 1, footnote d).

UiO-67-[Au]Cl was tested at 10% catalyst loading and gave moderate conversion (56%, 24 h, NMR scale, Table 1, entry 6). Notably, after 8 h, a pink discoloration was observed on the walls of the NMR tube. The pink material is suspected to be Au nanoparticles that originate from decomposition of the UiO-67-[Au]Cl catalyst. When the experiment was repeated at larger scale with stirring, high conversion was obtained (80%, 24 h, Table 1, entry 7). The heterogeneous nature of the catalyst was investigated by filtering the catalyst from the reaction mixture after stirring for 1 h. NMR monitoring of the filtrate showed that conversion of propargyl ester **3** continued the solid UiO-67-[Au]Cl was removed, indicating leaching of gold species into the solution, which gave moderate conversion (52%, 24 h). Reference reactions with



Scheme 2. (a) Cyclometalated complexes and Au(III)-MOF utilized in the current study; (b) propargyl ester cyclopropanation test reaction used to study the catalytic activity of the Au(III) species in the current study; (c) complexes studied before in the catalytic cyclopropanation reaction.

UiO-67 and UiO-67 with AuNPs gave no conversion (entries 8-9).

2.4. Cis and trans selectivity in NMR studies

In published reports, the *cis* isomer of the cyclopropanation product is usually formed, although subsequent *cis*-*trans* isomerization is observed with different rates dependent on the gold ligand and the substrate [37]. In contrast, all experiments with our neutral gold complexes gave high *trans* selectivity (up to 14:86 dr), and no further change in *cis:trans* ratio. The results indicate that our substituted ppy-ligands give a different stereoselectivity than other gold(III) complexes and are not active for *cis:trans* isomerization within the time span the reactions were carried out in (24 h). The cationic **2b**/AgOTf complex decomposed during the reaction and gave equal amounts of *cis* and *trans* isomers, supporting our theory that a different gold species is the catalytic species in this reaction.

2.5. Effect of reaction conditions on conversion. Recyclability of complex 2b

Monitoring of the integrity of the catalysts was possible during the catalytic runs by means of ¹H NMR and complex **2b** was observed to be intact after a reaction time of 24 h (see ESI). This observation prompted an investigation of the catalyst's recyclability. The experiments were scaled up and conversions evaluated with respect to modifications in the reaction conditions, and recovery of the catalyst was carried out



Fig. 5. Comparison of the catalytic activity of complexes 1a, 1b, 2a, and 2b.

after completion of the reaction. First, the experiment was investigated with respect to temperature and heating method (conventional or microwave) (Table 2). When the reaction was repeated at larger scale (108 mg propargyl ester 3, 30 mg complex 2b), the conversion was



UiO-67

UiO-67-[Au]Cl

Scheme 3. Post synthetic linker exchange in reaction between UiO-67 MOF and 2a under microwave heating in DMSO.

Table 1

Results from NMR studies of the gold-catalyzed cyclopropanation reaction between propargyl ester 3 and styrene (4).^a.

Entry	Catalyst	Conversion of 3 (1 h) [%]	Cis:trans (1 h)	Conversion of 3 (24 h) [%] (isolated yield in parenthesis)	Cis:trans (24 h)
1	1a	0	_	0	_
2	2a	17	32:68	45	23:77
3	1b	33	22:78	77 (80 ^b)	22:78
4	2b	43	10:90	97 (> 99)	16:84
5	2b /AgOTf	> 99 ^{c,d}	50:50	> 99	50:50
6	UiO-67-[Au] Cl	48	20:80	56	14:86
7	UiO-67-[Au] Cl	49	20:80	80 ^e	18:82
8	UiO-67	0	-	0	-
9	UiO-67@AuNPs [38]	0	-	0	-

^cApprox. 30% of species of unknown nature also generated within 1 h.

^dImmediate decomposition observed with similar observations when NaBAr^F and NaPF₆ were attempted.

^a Reagents and conditions: 5 mg of **3** with 11 μL of styrene with 10 mol% Au catalyst with 0.6 mL of CD₂Cl₂ in NMR tube at 21 °C. Conversions and *cis/trans* ratios were determined by ¹H NMR.

^b Dark precipitate in dark solution after 4 h observed.

^e Double scale compared to the NMR scale and stirred.

Table 2

Conversion dependence on reaction conditions for the scaled-up reaction between propargyl ester 3 and styrene (4) catalyzed by gold(III) complex 2b (10 mol%).

MeO	OAc + 2b	(10 mol%) DCM MeO	OAc		
Fatry	Heating source	Time	5 Temperature °C	Conversion of 3 %	cietrane
Entry	meaning source	Time	Temperature, C	Conversion of 3,70	<i>cis.u uns</i>
1	-	24 h	25	50	20:80
2	MW	30 min	100	79	20:80
3	MW	45 min	100	84	20:80
4	MW	1 h 30 min	85	85	20:80
5	MW	1 h 30 min	100	90 ^a	20:80
6	oil bath	9 h	55	> 95	20:80
7	oil bath	5 h	65	$> 95^{\mathrm{b}}$	20:80
8 ^c	oil bath	5 h	65	> 95 ^d	20:80

^a Decomposition of catalyst occurred.

^b Isolated yield 73%, cis/trans 26/74.

^c Recovered catalyst from entry 7.

^d Yield of cyclopropanated product 5 = 89% and was measured by ¹H NMR with dimethyl sulfone as internal standard.

Table 3

Recyclability of 2b .							
Cycle	1	2	3	4			
Conversion of 3, %	> 95	> 95	> 95	> 95			
Stability of 2b	yes	yes	yes	decomposed			

slower at r.t. and conversion was moderate after 24 h (50%, Table 2, entry 1). Utilization of microwave heating resulted in high conversions of the propargyl ester over short periods of time, but the reaction did not go to completion (79–85%, Table 2, entries 2–4). An increase in temperature and reaction time resulted in eventual decomposition of the gold catalyst, although high conversion of the substrate was obtained (90%, Table 2, entry 5). Further studies showed that heating in an oil bath at 65 °C for 5 h gave full conversion of propargyl ester **3** and generated the product **5** in high yield (Table 2, entry 7).

As anticipated, complex **2b** was stable (¹H NMR) under the selected conditions (Table 2, entry 7) and after full conversion of **3**, the isolation of complex **2b** was carried out by precipitating the complex from the reaction mixture with pentane. The recovery degree was found to be 93% (by mass) and the identity of complex **2b** was confirmed by ¹H NMR (see ESI). The recovered complex **2b** was subjected to a second round of catalyzing the cyclopropanation reaction and demonstrated the same level of activity giving high yield (89%, calculated by ¹H NMR using an internal standard, Table 2, entry 8). To our knowledge, reports

of the recyclability of Au(III) complexes are scarce and the catalytic ability and recyclability of complex **2b** is an exciting discovery [19,39].

Recyclability of complex **2b** *in situ* was also studied by conducting an experiment under the best conditions found, depicted in Table 2, entry 7. After 5 h, the substrate conversion was determined by ¹H NMR analysis and an additional 1 equivalent of propargyl ester **3** and 1 equivalent of styrene (**4**) was introduced to the reaction mixture. The reaction was repeated with an additional 3 cycles and the results are given in Table 3.

The cyclopropanation reaction catalyzed by **2b** could be repeatedly used for 3 cycles with no degradation of **2b**, which was observed only at the 4th cycle.

3. Conclusions

A convenient and robust method of synthesizing stable cyclometalated gold(III) complexes has been developed. Their structures have been confirmed through NMR and X-ray crystal analysis. The first Au (ppy)-functionalized linker has successfully been incorporated into the framework of MOF UiO-67. The resulting MOF has been analyzed by Xray spectroscopy analysis, ¹H NMR, TGA and nitrogen adsorption analysis. The results indicate the integrity of the Au(ppy) unit in the framework of UiO-67 MOF. NMR studies on the catalytic activity of the gold(III) complexes and Au–MOF were carried out in a known cyclopropanation reaction. Most of the catalysts showed moderate to excellent conversions on the NMR scale. When the reaction was scaled up with complex **2b**, the catalyst was found to be recoverable and recyclable in new reactions.

4. Experimental



4.1. Synthesis of 1a

The teflon liner for the microwave oven synthesis reactor was filled with gold(III) acetate (68 mg, 0.182 mmol, 1.1 equiv.), 6-(4-carbox-yphenyl)nicotinic acid (40 mg, 0.164 mmol, 1.0 equiv.) and trifluoroacetic acid (15 mL). The reaction mixture was heated in the microwave oven at $130 \degree$ C for 1 h. Still warm, the suspension was centrifuged and clear solution was decanted. The flask with solution was kept overnight in a dark place at room temperature until the crystalline product started to precipitate. The crystals were filtered and washed with water (until pH of the filtrate was 7), diethyl ester (10 mL) and dried under a stream of air giving the 50 mg of the complex **1a** as white solid (46% yield). X-ray-quality crystals were obtained by cooling the warm reaction mixture to room temperature.

Notes: material for NMR spectra was prepared by removing trifluoroacetic acid under reduced pressure immediately after the microwave synthesis and decomposes in solution over short period of time making spectra acquisition troublesome. Complex **1a** that precipitates out of the TFA solution is insoluble in DMSO- d_6 , DMF- d_7 and CD₃CN.

¹H NMR (400 MHz, DMSO-*d*₆): $\delta_{\rm H}$ 9.07–8.95 (m, 1H, *H*-5), 8.93–8.81 (m, 1H, *H*-3), 8.71–8.58 (m, 1H, *H*-4), 8.28–8.14 (m, 1H, *H*-4'), 8.13–8.00 (m, 1H, *H*-3'), 7.50 (s, 1H, *H*-5'). ¹H NMR (400 MHz, CD₃CN): $\delta_{\rm H}$ 9.10 (s, 1H, *H*-5), 8.81 (dd, *J* = 8.4, 1.8 Hz, 1H, *H*-3), 8.28 (d, *J* = 8.5 Hz, 1H, *H*-4), 8.13 (d, *J* = 8.0 Hz, 1H, H-4'), 7.90 (d, *J* = 8.0 Hz, 1H, *H*-3'), 7.62 (s, 1H, *H*-5'). ¹³C{¹H} NMR (151 MHz, DMSO*d*₆): $\delta_{\rm C}$ 165.2, 164.7, 163.2, 158.4 (q, CO, *J* = 37.9, 36.9 Hz), 148.1, 145.1, 145, 140.3, 133.4, 130.9, 128.4, 127.9, 127.2, 123.4, 115.7 (q, CF₃, *J* = 292.2, 290.3 Hz). ¹³C{¹H} NMR (151 MHz, CD₃CN): $\delta_{\rm C}$ 166.8, 165.5, 163.3, 158.9 (q, CO, *J* = 39.5 Hz), 150, 146.3, 146.1, 141.6, 134.2, 132.4, 129.3, 129.2, 128.4, 124.2 (signals of CF₃ group overlapped with solvent signal). MS (ESI⁺, CH₃OH): *m*/*z* 697.6582 [C₁₇H₈AuF₆NO₈ + CH₃OH]⁺ (calculated for C₁₄H₁₂AuF₆NO₉ 697.0080 (+0.65 ppm)).

4.2. Synthesis of 1b

The teflon liner for the microwave oven synthesis reactor was filled with gold(III) acetate (45 mg, 0.120 mmol, 1.2 equiv.), ethyl 6-(4(ethoxycarbonyl)phenyl)nicotinate (30 mg, 0.1 mmol, 1.0 equiv.) and trifluoroacetic acid (20 mL). The reaction mixture was heated in the microwave oven at 130 °C for 1 h. After cooling down to room temperature, the volatiles were removed in vacuum and solid crude was extracted with warm (40 – 45 °C) CH_2Cl_2 (2 × 15 mL). Combined fractions were filtrated through a folded filter and volume of the filtrate was reduced to 10 mL under vacuum. Product was precipitated as a white solid upon addition of the pentane (20 mL). The filtration resulted in 47 mg of **1b** as a white powder in 65% yield.

¹H NMR (600 MHz, CD₂Cl₂): $\delta_{\rm H}$ 9.23 (dd, *J* = 1.8, 0.6 Hz, 1H, *H*-5), 8.84 (dd, *J* = 8.4, 1.8 Hz, 1H, *H*-3), 8.16 (dd, *J* = 8.0, 1.4 Hz, 1H, *H*-3'), 8.11 (d, *J* = 8.4 Hz, 1H, *H*-4), 7.76 – 7.71 (m, 2H, *H*-4' and *H*-5'), 4.47 (q, *J* = 7.2 Hz, 2H, CH2(6)), 4.38 (q, *J* = 7.1 Hz, 2H, CH2(6')), 1.41 (dt, *J* = 19.0, 7.2 Hz, 6H, CH3(7 and 7')). ¹H NMR (400 MHz, DMSO-*d*₆): $\delta_{\rm H}$

9.03 (s, 1 H), 8.92 (dd, J = 8.4, 1.9 Hz, 1 H), 8.66 (d, J = 8.5 Hz, 1 H), 8.22 (d, J = 8.1 Hz, 1 H), 8.11 (dd, J = 8.1, 1.5 Hz, 1 H), 7.51 (s, 1 H), 4.42 (q, J = 7.2 Hz, 2 H), 4.35 (q, J = 7.0 Hz, 2 H), 1.34 (dt, J = 13.6, 7.1 Hz, 6 H).¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ_{C} 166.6 (C8), 164.3 (C1'), 161.8 (C1), 161.3 (CO, J = 37.8 Hz), 160.9 (CO, J = 39.3 Hz) 149.7 (CH-5), 145.6 (CH-3), 144.5 (C2), 141.6 (C8'), 134.8 (CH-2'), 131.9 (CH-3'), 129.4 (CH-4'), 129.0 (CH-5'), 127.1 (C8'), 122.7 (CH-4), 118.1 (CF3, J = 289.9 Hz), 116.1 (CF3, J = 288.4 Hz), 63.9 (-CH2-(6)), 62.7 (-CH2-(6')), 14.3 (CH-3(7)), 14.2 (CH-3(7')). ¹⁹F NMR (376 MHz, CD₂Cl₂): δ_{F} -77.05, -75.98. (ref. C₆F₆). MS (ESI⁺, CH₃OH): m/z 580.100 ([M-OAc^F-Et+H]⁺, 100%). Anal. calcd. for C21H16AuF6NO8: C, 34.97; H, 2.24; N, 1.94. Found: C, 33.77; H, 2.17; N, 1.87%.

4.3. Synthesis of 2a

The Teflon liner for the microwave oven synthesis reactor 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 (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. After the solvent removal, the solid crude was stirred with aqua regia solution (9 mL HCl and 3 mL HNO₃) for 30 min. The pale yellow precipitate was filtered through a fine frit, washed with water and dried under a stream of air for 30 min. The product was obtained in 87% yield (110 mg).

¹**H** NMR (600 MHz, DMSO-*d*₆): $\delta_{\rm H}$ 10.02 (d, *J* = 1.9 Hz, 1H, *H*-5), 8.78 (dd, *J* = 8.4, 1.9 Hz, 1H, *H*-3), 8.57 (d, *J* = 8.5 Hz, 1H, *H*-4), 8.33 (d, *J* = 1.5 Hz, 1H, *H*-5'), 8.15 (d, *J* = 8.1 Hz, 1H, *H*-4'), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H, *H*-3'). ¹³**C** NMR (151 MHz, DMSO-*d*₆): $\delta_{\rm C}$ 165.9 (C1'), 165.5 (C8), 163.8 (C1), 151.1 (C2'), 149.1 (CH-5), 145.9 (C8'), 143.9 (CH-3), 133.3 (C9), 130.3 (CH-5'), 129.9 (CH-3'), 128.1 (C2), 127.6 (CH-4'), 122.9 (CH-4). MS (ESI⁺, CH₃OH): *m*/z 531.939 ([³⁵M + Na]⁺, 100%), 533.936 ([^{35/37}M + Na]⁺, 63.7%), 535.933 ([³⁷M + Na]⁺, 10.6%). HRMS (ESI⁺, CH₃OH): *m*/z 531.9386 (calculated for C₁₃H₈AuCl₂NNaO₄ 531.9388 (+0.5 ppm)). Anal. calcd. for C13H8AuCl2NO4: C, 30.61; H, 1.58; N, 2.75. Found: C, 30.12; H, 1.63; N, 2.71%.

4.4. Synthesis of 2b

The teflon liner for the microwave oven synthesis reactor was filled with gold(III) acetate (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. The volatiles were removed under reduced pressure and afforded Au(ppyde)(OAc^F)₂ as a pale-yellow solid which was used without further purification. The crude was then taken up with aqua regia solution (9 mL HCl and 3 mL HNO₃) for 30 min. The pale yellow precipitate was filtered through a fine frit, washed with water and dried under a stream of air for 30 min. The product was obtained in 80% yield (90 mg).

¹H NMR (600 MHz, DMSO- d_6): δ_H 10.06 (d, J = 1.9 Hz, 1H, H-5), 8.84 (dd, J = 8.4, 2.0 Hz, 1H, H-3), 8.63 (d, J = 8.4 Hz, 1H, H-4), 8.39 (d, J = 1.6 Hz, 1H, H-5'), 8.23 (d, J = 8.1 Hz, 1H, H-4'), 8.04 (dd, J)J = 8.0, 1.6 Hz, 1H, H-3'), 4.44 (q, J = 7.1 Hz, 2H, H-6), 4.37 (q, J=7.1 Hz, 2H, H-6'), 1.36 (dt, J = 14.3, 7.1 Hz, 6H, H-7 and 7'). ¹H **NMR** (600 MHz, CDCl₃): $\delta_{\rm H}$ 10.41 (d, J = 1.8 Hz, 1 H), 8.78 (dd, J = 8.4, 1.8 Hz, 1 H), 8.67 (d, J = 1.4 Hz, 1 H), 8.12 (dd, J = 8.1, 1.5 Hz, 1 H), 8.07 (d, J = 8.4 Hz, 1 H), 7.72 (d, J = 8.1 Hz, 1 H), 4.52 (q, J = 7.1 Hz, 2 H), 4.44 (q, J = 7.1 Hz, 2 H), 1.45 (dt, J = 19.8, 7.1 Hz, 7 H). ¹³C{¹H} NMR (151 MHz, DMSO-*d*₆): δ_C 165.7 (*C*1), 164.4 (*C*1'), 162.3 (C8), 151.0 (C9), 148.8 (CH-5), 146.2 (C8'), 143.8 (CH-3), 132.3 (C2'), 129.9 (CH-5'), 129.8 (CH-3'), 127.9 (CH-4'), 127.1 (C2), 123.1 (CH-4), 62.4 (CH₂(6)), 61.6 (CH₂(6')), 14.14 (CH₃(7)), 14.06 (CH₃(7')). **MS** (ESI⁺, CH₃OH): m/z 588.002 ([M+Na⁺], 7%), 584.051 ([M $+H_3O^+$], 100%). HRMS (ESI⁺, CH₃OH): calculated for $C_{17}O_4H_{16}AuNCl_2Na^+$ [*M*+Na⁺] 588.0014, found 588.0016 (Δ -0.2 ppm). Anal. calcd. for C17H16AuCl2NO4: C, 36.06; H, 2.85; N, 2.47. Found: C, 35.78; H, 2.90; N, 2.43%.

4.5. Synthesis of 3

To a stirred ethynylmagnesium bromide solution (38 mL of 0.5 M solution in THF, 19 mmol) on ice bath, a solution of p-anisaldehyde (2 g, 14.69 mmol) in THF (5 mL) was added under nitrogen atmosphere. Solution was stirred for 15 min on ice bath and overnight at room temperature. Water (50 mL) with Et₂O (40 mL) were added and the organic phase was separated. The aqueous phase was extracted with Et₂O (2×40 mL) and the combined phases were dried with Na₂SO₄. Filtration followed by solvent removal under reduced pressure resulted in 1-phenylprop-2-yn-1-ol as a viscous, yellow-brown oil which was used for next step without further purification. Mixture of 1-phenylprop-2-yn-1-ol (2.17 g, 13.38 mmol) acetic anhydride (3.6 mL) and trimethylamine (5.3 mL) in DCM (20 mL) was stirred at room temperature overnight. The solution was poured into 1 M NaOH until pH = 14 and mixed with DCM (25 mL). After the organic layer was separated, the compound was extracted with DCM ($2 \times 25 \text{ mL}$). The combined organic layer was dried over Na₂SO₄, filtered off, and purified by column chromatography using ethyl acetate/hexane mixture (1:10) as an eluent. The obtained pale-yellow oil solidified in the freezer. Yield: 2.43 g, 81%. The compound must be stored in the freezer under vacuum in a Schlenk flask.

4.6. Synthesis of UiO-67[Au]Cl

A mixture of UiO-67 MOF (200 mg) and **2a** (67 mg, 0.118 mmol) in DMSO (8 mL) was heated at 85 °C for 6 h in the microwave oven. The resulted powder was washed with hot DMSO (3 times) and acetone (3 times). The material was then dried under dynamic vacuum overnight yielding UiO-67[Au]Cl (240 mg). Anal. calcd. for C83H52AuCl2NO32Zr6 (corresponds to Zr6O4(OH)4(C14H8O4) 5(C13H8AuCl2NO4)): C, 41.70; H, 2.19; N, 0.59; Au, 8.24; Zr, 22.90. Found: C, 41.51; H, 2.17; N, 0.58; Au. 8.20; Zr, 22.81%.

4.7. Digestion of MOF

Digestion solution: To 54 mg of D_3PO_4 (86% in D_2O) was added 3.3 mL DMSO- d_6 (for 1 mL of DMSO- d_6 was used 18 mg of 86% D_3PO_4).

Procedure: To 15 mg of MOF material 600 μ L of digestion solution added and sonicated for 1 min. The suspension was then placed on a shaker and left overnight. The suspension was then placed in the NMR tube and the ¹H NMR spectrum recorded.

4.8. General procedure for catalysis

Catalytic tests were carried out following published procedure. [37] A mixture of **3** (5 mg, 0.024 mmol, 1 equiv.) and styrene (11 μ L, 0.096 mmol, 4 equiv.) in CD₂Cl₂ (0.6 mL) was added to the gold catalyst. The reaction's development was monitored by ¹H NMR at 10 min, 1 h, 2 h, 4 h, 8 h, 16 h and 24 h.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Volodymyr A. Levchenko: Investigation, Methodology, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. Huey-San Melanie Siah: Investigation, Methodology, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Sigurd Øien-Ødegaard:** Investigation, Formal analysis, Validation, Visualization. **Gurpreet Kaur:** Investigation, Formal analysis, Validation, Visualization. **Anne Fiksdahl:** Supervision, Resources, Methodology, Conceptualization, Writing - review & editing. **Mats Tilset:** Supervision, Resources, Methodology, Conceptualization, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111009.

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V.A. Levchenko, et al.

Molecular Catalysis 492 (2020) 111009

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