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Gold(I) complexes bearing a PNP-type pincer ligand: photophysical properties and catalytic investigations†

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The synthesis and characterization of two dinuclear and five tetranuclear gold(I) complexes bearing the 2,6-bis(diphenylphosphinomethyl)pyridine diphosphane ligand (DPPMPY) are herein reported. The reaction between the dinuclear complexes, DPPMPY(AuCl)$_2$ (**1**) or DPPMPY(AuBr)$_2$ (**2**), with 1 or 2 equivalents of Ag salts yielded five tetranuclear gold(I) complexes, DPPMPY$_2$Au$_4$X$_2$ (**3–7**), differing in the terminal ancillary ligands (X = Cl, Br, acetonitrile) and the counter ions (SbF$_6^-$ or BF$_4^-$). The structures of complexes **1**, **2**, **3**, and **5** were confirmed by single-crystal X-ray diffraction studies. The Au⋯Au distances found in complexes **3** and **5** are in the range of aurophilic interactions and the arrangement of the Au atoms varies from a linear arrangement in complex **3** to a zigzag arrangement in complex **5**. The photophysical characterization of the compounds was performed both in solution and in the solid state. Very high emission quantum yields were observed for the acetonitrile complexes **4** and **6** in the solid state. The use of this family of gold(I) complexes as catalysts for lactone synthesis via oxidative heteroarylation of alkenes was investigated and yields up to ca. 65% were obtained. Dicationic halide complexes **3** and **5** showed a slight enhancement of the yield of the catalytic reaction, indicating that there is no influence of the counter ion employed on the reaction outcome. Luminescence techniques have been also used to follow the progress of the catalytic reaction.

Introduction

Luminescent compounds are of great interest because of their multifaceted use in different research topics such as probes for biological applications, molecular sensors and opto-electronic devices.[1] In particular, luminescent metal complexes with relatively high emission quantum yields have attracted considerable attention as light-emitting molecular based devices.[2] The intrinsic luminescence of metal complexes may arise because of and be affected by several factors, such as the chromophore, ancillary ligands, geometry, rigidity, solvent,

counter ions, type of metal and, in some particular metals (mainly those with a d^8 or d^{10} configuration), metal⋯metal interactions. The latter metallophilic contacts also facilitate supramolecular assemblies that enhance the photoluminescent properties. For example, gold complexes with aurophilic interactions are especially interesting due to their potential applications in a wide array of disciplines, including biology, optical sensors, supramolecular chemistry and photochromism.[3]

Gold-based catalysis is another well-known application of this type of complex and is recognized as a popular topic in organic synthesis.[4] In particular, polynuclear gold(I) complexes with aurophilic contacts have received increasing attention since their cooperative properties and reactivity have been evidenced in a variety of catalytic processes (Scheme 1):[5] (i) cycloisomerization of low-substituted 1,6-enynes;[6] (ii) intramolecular hydroamination of a urea-functionalized alkyne;[7] (iii) carbonylation of primary amines to form ureas;[8] and (iv) oxidative heteroarylation of alkenes.[9]
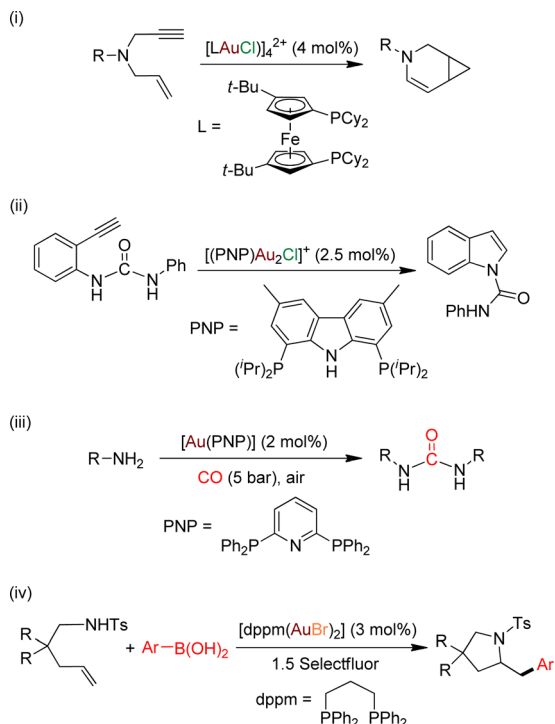
Taking these precedents into consideration, we decided to synthesize di- and tetranuclear gold(I) complexes bearing the 2,6-bis(diphenylphosphinomethyl)pyridine ligand (DPPMPY) in order to study the impact of the flexibility of the ligand on the structural features of the gold complexes and their lumine-

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†Electronic supplementary information (ESI) available. CCDC 2168662, 2168663 and 2168683. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2dt02429b
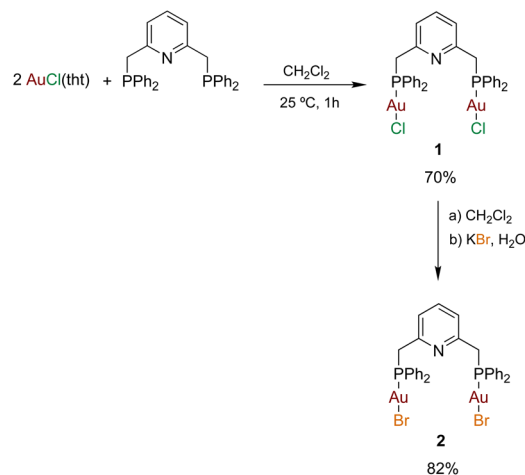
Scheme 1 Selected examples of reactions by polynuclear gold(I).

Scheme 2 Synthesis of complexes DPPMPY(AuCl)$_2$, **1**, and DPPMPY (AuBr)$_2$, **2**.

Fig. 1 Crystal structure of complex DPPMPY(AuCl)$_2$, **1**. Hydrogen atoms and dichloromethane molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Au(1)–P(1), 2.2366(7); Au(2)–P(2), 2.2320(6); Au(1)–Cl(1), 2.3078(7); Au(2)–Cl(2), 2.3078(8); Cl(1)–Au(1)–P(1), 175.60(2); Cl(2)–Au(2)–P(2), 177.17(2).

scence properties. Following previous developments reported by Echavarren[8] and Toste,[9] we decided to study the catalytic activity of these complexes for oxidative heteroarylation of alkenes to obtain lactones[10] since these compounds are embedded within the structure of bioactive natural products[11] with biological functions.[12]

Results and discussion

Synthesis and structure of DPPMPY gold(I) complexes

The mononuclear DPPMPY(AuCl)$_2$ complex **1** was synthesized by the reaction of [AuCl(tht)] with DPPMPY (DPPMPY = 2,6-bis (diphenylphosphinomethyl)pyridine) in a 2 : 1 ratio in CH$_2$Cl$_2$ (Scheme 2) at room temperature. This complex was characterized by NMR spectroscopy. For example, a doublet is observed at 4.04 ppm ($^2J_{HP}$ = 12.7 Hz) corresponding to the four equivalent protons of the methylene groups of the DPPMPY ligand in the ^{1}H NMR spectrum (see ESI†). Accordingly, a single resonance appears at 33.4 ppm for the two equivalent phosphorus nuclei in the ^{31}P{^{1}H} spectrum. The structure of **1** was confirmed by single-crystal X-ray diffraction (Fig. 1). The Au⋯Au distance (3.3558(4) Å) is less than the sum of the van der Waals radii (3.6 Å),[13] similar to that found for the gold(I) complex bearing the PNP ligand (PNP = pyridine-2,6-diylbis (diphenylphosphino)methanone, 2,6-{Ph$_2$PC(O)}$_2$(C$_5$H$_3$N)).[14] The gold-phosphorus and gold-chloride bond lengths are in the range of those reported previously for other gold–phosphine complexes.[7,14,15] Both P(1)–Au(1)–Cl(1) and P(2)–Au(2)–Cl(2) bond angles are close to the typical linear coordination.[15]

The bromine complex, DPPMPY(AuBr)$_2$, **2**, was obtained by treating a solution of **1** in CH$_2$Cl$_2$ with an aqueous solution of potassium bromide (Scheme 2). The NMR spectroscopic data of **2** were similar to those described above for **1**. Thus, the ^{1}H NMR spectrum shows a doublet at 4.09 ppm ($^2J_{HP}$ = 12.7 Hz) and a singlet at 35.1 ppm is observed in the ^{31}P{^{1}H} NMR spectrum. X-ray quality crystals were grown for **2**. Fig. 2 depicts the structure of this complex. The Au⋯Au distance (3.7798(4) Å) found for **2** is longer than in the case of **1**, which may be due to the halide influence. The gold–bromide bond distances are in the range normal for this type of compound.[16] The other structural characteristics of **2** are similar to those described for **1** and do not deserve further discussion.

Subsequently, **1** was reacted with 1 or 2 equivalents of AgSbF$_6$ in CH$_2$Cl$_2$ or a mixture of CH$_2$Cl$_2$/CH$_3$CN at room temperature to generate tetranuclear complexes **3** and **4** in good yields (Scheme 3). Analogous to other similar tetranuclear [(Ph$_2$P)$_2$Py]gold(I) compounds previously described by Echavarren and co-workers ([(Ph$_2$P)$_2$Py] = (2,6(diphenylphosphino)pyridine)),[8] both complexes show fluxional behavior. Therefore, the ^{1}H NMR spectrum of **3** shows two broad signals
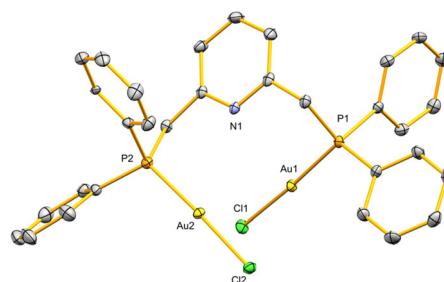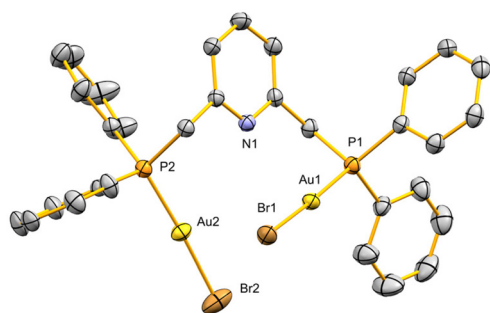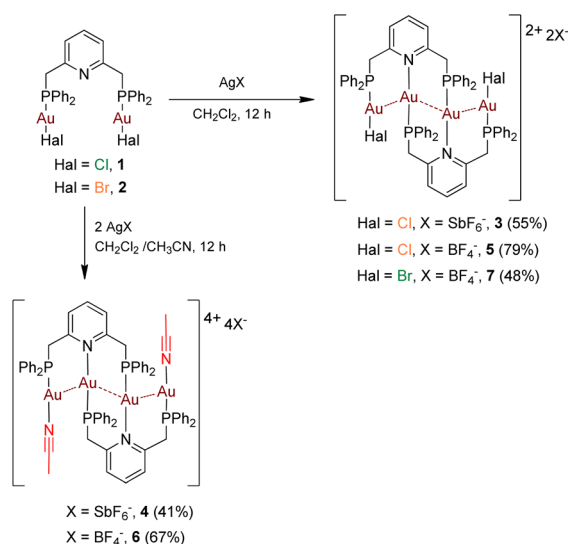
Fig. 2 Crystal structure of the complex DPPMPY(AuBr)$_2$, **2**. Hydrogen atoms and dichloromethane molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Au(1)−P(1), 2.239(1); Au(2)−P(2), 2.232(1); Au(1)−Br(1), 2.4128(6); Au(2)−Br(2), 2.4057(7); Br(1)−Au(1)−P(1), 176.30(3); Br(2)−Au(2)−P(2), 176.51(4).

Scheme 3 Synthesis of tetranuclear complexes **3–7**.

at 4.62 and 4.25 ppm due to the two chemically inequivalent methylene groups attached to the phosphorus (ESI†).

In good agreement with these observations, in the ^{31}P{^{1}H} NMR spectrum, two broad singlets are observed at 35.0 and 28.0 ppm due to the two types of inequivalent phosphorus nuclei in the molecule. Analogously, **4** displays two very broad signals that appear at 4.98–4.74 and 4.48–4.18 ppm corresponding to the methylene protons in the ^{1}H NMR spectrum and two resonances are observed at 30.4 and 25.6 ppm in the ^{31}P{^{1}H} NMR spectrum. The structure of **3** was analysed by a single-crystal X-ray study (ESI†). The poor diffraction of the crystals and the polycrystalline nature of the sample make the structure not suitable for publication, although some structural aspects can be discussed. The molecular structure of **3** seems to be an almost linear string arrangement of four Au atoms connected by three Au–Au contacts involving aurophilic interactions.[17]

Tetranuclear complexes with BF$_4^-$ as the counter anion, **5** and **6**, were prepared using AgBF$_4$ following the procedure

described in the ESI† (Scheme 3). The spectroscopic characteristics of these two complexes were similar to those of complexes **3** and **4**, so they do not deserve further discussion (ESI†). The crystallographic structure of **5** is shown in Fig. 3. In contrast to **3**, complex **5** presents a zigzag arrangement of the four gold atoms with a small intermetallic angle of 95.6(0)°.[18] This observation is in concordance with previously reported data that showed that the counter anion may influence the type of arrangement adopted in the molecule, which can also affect[19] the photoluminescence properties of the complexes in the solid state.[20] The external Au⋯Au distances, A1–A2 and A3–A4 (*ca.* 3.2880 Å) are longer than the internal one, A2–A3 (2.9904(9) Å). The other bond distances and angles are similar to other previously reported PNP-gold(ı) complexes[8] (see the ESI†).

Finally, the complex [DPPMPY$_2$Au$_4$Br$_2$][BF$_4$]$_2$ **7** (Scheme 3) was obtained by a similar procedure to that for complex **5** (see the ESI for its synthesis and characterization†).

Photophysical characterization

The photophysical properties of the DPPMPY-gold complexes were studied. First, absorption and emission spectra were recorded in 1 × 10^{-5} M dichloromethane solutions and the results are summarized in Table 1. The absorption spectra of all the compounds display a band at *ca.* 275 nm that can be attributed to intraligand π–π* transitions of the aromatic rings
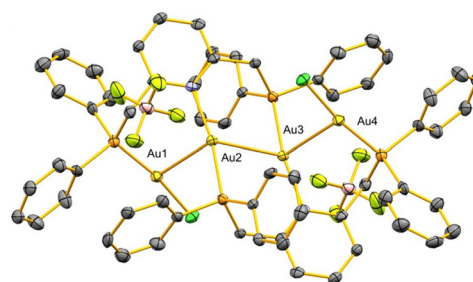

Fig. 3 Crystal structure of complex [(DPPMPY)$_2$(Au$_4$Cl$_2$)][BF$_4$]$_2$, **5**. Hydrogen atoms are omitted for clarity. Structure (a) with the BF$_4^-$ anion and (b) with the BF$_4^-$ anion are omitted. Selected bond distances (Å) and angles (°): Au1–Au2, 3.288(0); Au2–Au3, 2.9904(9); Au3–Au4, 3.288(3); Au1–Au2–Au3, 95.7(1); Au2–Au3–Au4, 95.6(0).

Table 1 Absorption and emission data of the compounds in dichloromethane at 1 × 10^{-5} M (λ_{exc} = 350 nm) and in the solid state

| Complex | Solution | | Solid |
	λ_{max} Abs, nm (ε, cm^{-1} M^{-1} 10^3)	λ_{max} E_m, nm (N$_2$-sat)	λ_{max} E_m, nm
1	270 (17.77)	— (403, 545)	—
2	271 (13.13)	—	—
3	275 (24.71), 350 (12.90)	513 (404, 513)	504
4	278 (31.60), 350 (20.74)	496 (496)	500
5	278 (29.31), 350 (18.91)	515 (404, 515)	508
6	277 (55.38), 350 (28.61)	498 (405, 498)	510
7	271 (22.87), 350 (5.72)	514 (401, 514)	—

of the DPPMPY phosphane (Fig. S1 and 2†). A second band at 350 nm is only present in the tetranuclear complexes **3–6** and can be attributed to spin allowed Au(d) → Au(p) transitions such as $5d_{\sigma^*} \rightarrow 6p_{\sigma}$ and singlet MLCT transitions.[21] The energy levels of these excited states are expected to be directly affected by the cluster core structure, the Au···Au interactions and the ligands.[1] Excitation of air-equilibrated samples at 350 nm gave rise to a broad emission band centred around 500–515 nm for all tetranuclear compounds in solution. This is also recorded in the solid state for compounds **3–6** (Fig. 4 and S4†). This emission band can arise from the mixed nature LMCT/ LMMCT + metal centred transitions and is more favoured in the solid state with quantum yields one order of magnitude larger.[22] The large Stokes shift and lifetimes in the order of microseconds (Table 2) support a triplet state origin and, therefore, phosphorescence emission. Dual emission (fluorescence + phosphorescence) is observed for **3**, **5** and **7** when the oxygen is removed from the solution (N$_2$-saturated) with the presence of a new fluorescence intraligand emission band (^{1}IL) at *ca.* 400 nm (Fig. S4†). Only fluorescence emission can be detected for the dinuclear precursor **1** when oxygen is removed from the solution, while no significant emission was recorded for the analogous dinuclear bromide complex **2**. The gold(I) terminal ancillary ligand halide or acetonitrile ligands have some influence on the emission maxima. The maxima for the halide complexes, **3**, **5** and **7**, were *ca.* 20 nm redshifted with respect to their analogous compounds containing acetonitrile. No significant effect of the counter anion can be

observed in solution, while it seems to have a greater effect in the solid state where closer contacts may be expected for BF$_4^-$ derivatives **5** and **6**, with more red-shifted emission, in agreement with the closer contact of this counter anion with respect to SbF$_6^-$ observed in the X-ray crystal structure data. Interestingly, the metal centred emission band at 500 nm is the only dominating emission pathway in the solid state for **3–6**, as expected for more efficient packing and close contact of the metal centres. This band cannot be detected for dinuclear compounds **1** and **2** or for the bromide tetranuclear complex **7** (Fig. 4).

Emission lifetime values collected at 550 nm exhibit biexponential decays with a major component around 0.5–1 μs (with >95% amplitude) in solution (Table 2). The minor component presents a lifetime value around 6 μs that corresponds to the parent compound **1** that could be formed from some decomposition of the tetranuclear compounds during the measurements. These behaviours are similar to those previously reported for other phosphane gold(I) complexes.[2–4,22,23] Lifetime values become much larger, about 100 μs, in the solid state. The quantum yields recorded in the solid state are much larger than in solution, as previously reported for other analogous compounds.[23] Of particular note are the values of **4** (64%) and **6** (44%), making the compounds promising for the development of highly emissive materials.

The radiative and non-radiative rate constants, k_r and k_{nr}, were calculated from φ and τ (see Table S2†), and we can observe that the increase in quantum yields is due to a decrease in the k_{nr} values in deoxygenated samples in solution, and mainly in the case of acetonitrile derivatives **4** and **6** in the solid state.

Catalytic activity of the DPPMPY-gold(I) complexes

Gold(I) complexes bearing diphosphane ligands have been successfully used as catalysts in different systems, such as homogeneous carbonylation of amines,[8] intramolecular hydroalkoxylation reactions of allenes,[24] hydroamination of allenes,[25] conjugated diene hydroamination,[26] oxidative reactions of propargylic acetates and benzoates,[27] and intramolecular aminoarylation of alkenes.[9] Previously to these catalytic systems, Hashmi and coworkers studied oxidative coupling using organogold(I) compounds and several electrophiles commonly employed in gold catalysis.[28] In the case of intramolecular
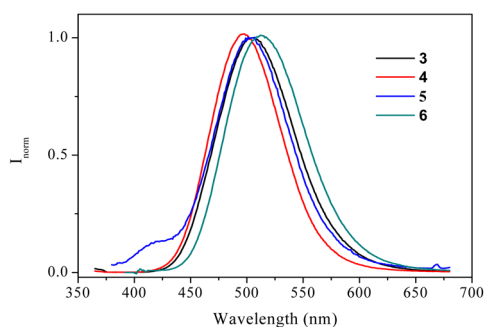

Fig. 4 Normalized emission spectra of the tetranuclear complexes in the solid state (λ_{exc} = 350 nm).

Table 2 Lifetimes (τ) and quantum yields (φ) recorded in air-equilibrated and N$_2$ saturated solutions and in the solid state together with the calculated radiative (k_r) and non-radiative (k_{nr}) rate constants

Compound	Solution				Solid state			
	τ (air eq./N$_2$ sat, μs)	φ (air eq./N$_2$ sat)	k_r (air eq./N$_2$ sat)	k_{nr} (air eq./N$_2$ sat)	τ (μs)	φ	k_r	k_{nr}
1	—/5 × 10^{-3}	—/0.042	—/9.77E6	—/2.23E8	—	—	—	—
2	—/—	—/—	—/—	—/—	—	—	—	—
3	0.3/0.6	0.01/0.02	3.24E4/2.95E4	2.92E6 /1.70E6	126	0.16	1.29E3	6.66E3
4	0.4/0.9	0.01/0.02	2.75E4/2.00E4	2.47E6 /1.16E6	139	0.64	4.60E3	2.59E3
5	0.3/0.6	0.01/0.02	2.62E4/2.52E4	2.89E6/1.77E6	101	0.13	1.22E3	8.68E3
6	0.3/0.7	0.01/0.03	4.00E4/4.09E4	3.29E6 /1.42E6	100	0.44	4.36E3	5.57E3
7	0.06/0.09	0.006/0.01	1.00E5/8.89E4	1.66E7/1.10E7	—	—	—	—

aminoarylation of alkenes, the Toste group carried out a mechanistic study to explain why the dinuclear [dppm(AuBr)$_2$] (dppm = diphenylphosphinemethane) complex showed better catalytic activities than mononuclear gold complexes. The results of these investigations seemed to indicate that a possible aurophilic interaction could regulate the redox potential of the dinuclear gold complex, making the process more accessible than in the case of mononuclear complexes.[9] Based on this latter contribution, we decided to test the catalytic capacity of the DPPMPY-gold(I) complexes in the intramolecular arylation of alkenes, but instead of using a sulfonamide (Scheme 1, iv), the commercially available 2-vinylbenzoic acid was employed to obtain the lactone derivative (Table 3). In our study, we intended to compare the performance of the dinuclear and tetranuclear complexes. We initially tested the catalytic capabilities of complex **1** in the reaction of 2-vinylbenzoic acid with 1 equivalent of phenylboronic acid[29] and 1.5 equivalents of Selectfluor in MeCN at room temperature. Only a 15% yield was obtained after 18 h (entry 1). The yield was improved upon increasing the reaction temperature (entries 2 and 3), with the optimum yield obtained at 70 °C (50%). The possible participation of gold nanoparticles was ruled out since the mercury test gave a negative result (see the ESI†). We then studied the rest of the DPPMPY-gold complexes as catalysts under the latter conditions. The yield with the bromide dinuclear complex **2** was comparable to that obtained with **1** (52%, entry 5). Therefore, in contrast to the observations of Toste and co-workers,[9] the coordinated halide has a nonsignificant effect on the reaction outcome. Higher yields were obtained when using the dicationic complexes **3** and **5** as catalysts (55 and 61%, entries 5 and 6), which shows that the

counter anion employed does not have an important influence. The slight enhancement of the yield in the case of the dicationic complexes is perhaps due to a more facile oxidation of the aurophilic Au(I)–Au(I) complexes with Selectfluor as previously proposed by Toste and co-workers. As already observed in the case of **1**, the yield was reduced when the reaction was carried out at room temperature or 40 °C in the presence of **5** (entries 7 and 8). Tetracationic complexes **4** and **6** (entries 9 and 10, respectively) showed activities similar to those of **3** and **5**. As already observed for the neutral complexes, the coordinated anion does not influence the catalytic performance as inferred from the result obtained when complex [DPPMPY$_2$Au$_4$Br$_2$][BF$_4$]$_2$ **7** was used as a catalyst (entry 11). In addition, we compared the catalytic performance of the DPPMPY-gold complexes with those of dinuclear [dppm(AuCl)$_2$] and [dppm(AuBr)$_2$] used by the Toste group in this type of system (entries 12 and 13). The yields were similar to those obtained with our tetranuclear complexes **3–7**, which shows the potential application of these complexes for other oxidative arylation processes. The reaction yield was very low in the absence of the catalyst at 70 °C. Finally, with the aim to evaluate the impact of the gold loading on the reaction outcome, two different reactions were performed (entries 15 and 16). The first one was carried out with 6 mol% of complex **1** as catalyst, while 1.5 mol% of complex **7** was used in the second one. Yields of 56% and 50% were obtained, respectively. These results suggest the participation of a similar intermediate in the reaction regardless of whether a dinuclear or a tetranuclear complex was used as a catalyst precursor.

In order to gather some information about possible similar intermediates in the catalytic process we performed the reaction of **1** and **7** with 10 equivalents of Selectfluor at room temperature. In both cases two new peaks (ratio 1 : 1) were observed in the ^{31}P{^{1}H} NMR of the reaction mixture (see the ESI†), which could suggest the formation of tetranuclear species. The chemical shift moved to higher frequencies, possibly due to gold oxidation as described by Toste.[9]

Catalytic assays followed by luminescence

The intrinsic luminescence properties of the final lactone product (see ESI†) encouraged us to use emission as a tool to detect the reaction progress and success. In this way, we chose the best experimental conditions previously found (acetonitrile, 70 °C and same % of catalyst) and the reaction was followed by recording emission spectra of the solution mixture at different times. Fortunately, we could identify the formation of the lactone with the appearance of an emission band at *ca.* 430 nm corresponding to this species almost immediately after 1 h of reaction, and the emission intensity was observed to increase up to 24 h of reaction (Fig. 5). Importantly, the low emission intensities of the catalysts in solution do not overlap the emission of the lactone and make these compounds ideal candidates for this type of experiment.

Interestingly, monitoring catalytic reactions through emission experiments can become an advantageous methodology due to the high sensitivity of this technique.

Table 3 Study of the oxyarylation reaction catalyzed by DPPMPY-gold (I) complexes

Entry	Catalyst	Yield^a (%)	T (°C)
1	**1**	15	RT
2	**1**	30	40
3	**1**	50	70
4	**2**	52	70
5	**3**	55	70
6	**5**	61	70
7	**5**	23	RT
8	**5**	40	40
9	**4**	54	70
10	**6**	60	70
11	7	61	70
12	dppm(AuCl)$_2$	51	70
13	dppm(AuBr)$_2$	63	70
14	—	0	70
15^b	**1**	56	70
16^c	**7**	50	70

^{a} Yields obtained by ^{1}H NMR spectroscopy of the reaction mixture (triphenylmethane as internal calibration standard). ^{b} 6 mol%. ^{c} 1.5 mol%.
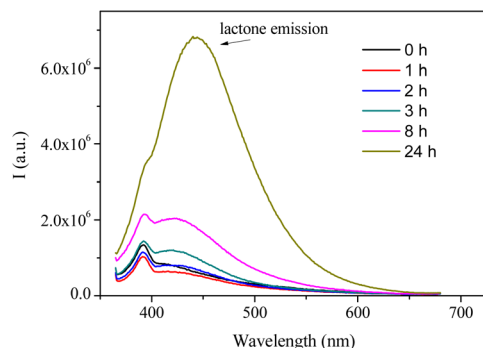
Fig. 5 Emission spectra of the catalytic reaction using complex **3** as a catalyst at different times. Experimental conditions: 70 °C, acetonitrile, Selectfluor (1.5 equivalents) and **3** (3%).

Conclusions

Tetranuclear gold(ɪ) complexes containing aurophilic interactions have been synthesized with the ligand DPPMPY. Single-crystal X-ray diffraction studies have shown that the arrangement of Au atoms varies from a linear to a zigzag arrangement depending on the counteranion. Di- and tetranuclear gold(ɪ) complexes containing DPPMPY ligand are a good choice for use as catalysts in oxyarylation reactions with moderate-high yields. The core, consisting of Au···Au contacts, may play a direct role in the catalytic behaviour. Additionally, the terminal ancillary ligands also affect the catalytic activity with better results for the compounds containing a halide at the terminal position.

Strong luminescence has been recorded for the compounds in the solid state, mainly for the tetracationic compounds, *i.e.*, those containing acetonitrile at the terminal position, being excellent candidates for luminescent materials. On the other hand, their low emission quantum yields recorded in solution introduce a new possibility to control the progress of catalytic reactions for the synthesis of aromatic compounds that can display intrinsic luminescence (such as lactones). This method is promising as a first attempt to monitor the progress of a catalytic reaction using very small quantities of catalysts.

Author contributions

M. C. and G. R.-I. contributed equally to this work.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

References

1 (*a*) Z. Qin, C. Gao, W. W. H. Wong, M. K. Riede, T. Wang, H. Dong, Y. Zhen and W. Hu, *J. Mater. Chem. C*, 2020, **8**, 14996–15008; (*b*) X. Yang, G. Zhou and W. Y. Wong, *Chem. Soc. Rev.*, 2015, **44**, 8484–8575.

2 (*a*) C. Fan and C. Yang, *Chem. Soc. Rev.*, 2014, **43**, 6439–6469; (*b*) R. C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093–2126.

3 (*a*) M. C. Gimeno and A. Laguna, *Silver and Gold. Comprehensive Coordination Chemistry II*, ed. J. A. MacCleverty and T. J. Meyer, Elsevier, Pergamon, New York, 2003, vol. 6, p. 911; (*b*) *Modern Supramolecular Gold Chemistry*, ed. Laguna, A. Wiley-WCH, 2008; (*c*) H. E. Abdou, A. A. Mohamed and J. P. Fackler Jr., *Gold Chemistry: Applications and Future Directions in the Life Sciences*, ed. F. Mohr, Wiley-WCH, 2009; (*d*) J. C. Lima and L. Rodríguez, *Chem. Soc. Rev.*, 2011, **40**, 5442–5456; (*e*) M. Pujadas and L. Rodríguez, *Coord. Chem. Rev.*, 2020, **408**, 213179; (*f*) A. Pinto, N. Svahn, J. C. Lima and L. Rodríguez, *Dalton Trans.*, 2017, **46**, 11125–11139.

4 (*a*) M. Haruta, *Nature*, 2005, **437**, 1098–1099; (*b*) S. P. Nolan, *Acc. Chem. Res.*, 2011, **44**, 91–100; (*c*) M. Mato, A. Franchino, C. García-Morales and A. M. Echavarren, *Chem. Rev.*, 2021, **121**, 8613–8684; (*d*) E. Jimenez-Núñez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326–3350; (*e*) Z. Li, C. Brouwer and C. He, *Chem. Rev.*, 2008, **108**, 3239–3265; (*f*) A. S. K. Hashmi and M. Rudolph, *Chem. Soc. Rev.*, 2008, **37**, 1766–1775; (*g*) C. Nieto-Oberhuber, M. P. Muñoz, S. Lopez, E. Jimenez-Nuñez, C. Nevado, H.- E. Gomez, M. Raducan and A. M. Echavarren, *Chem. – Eur. J.*, 2006, **12**, 1677–1693; (*h*) M. Rudolph and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2012, **41**, 2448–2462; (*i*) X. Zhao, M. Rudolph and A. S. K. Hashmi, *Chem. Commun.*, 2019, **55**, 12127–12135; (*j*) L. Huang, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2016, **55**, 4808–4813; (*k*) L. Huang, F. Rominger, M. Rudolph, A. Stephen and K. Hashmi, *Chem. Commun.*, 2016, **52**, 6435–6438; (*l*) M. Rigoulet, O. Thillaye du Boullay, A. Amgoune and D. Bourissou, *Angew. Chem., Int. Ed.*, 2020, **59**, 16625–16630; (*m*) J. Rodriguez, A. Tabey, S. Mallet-Ladeira and D. Bourissou, *Chem. Sci.*, 2021, **12**, 7706–7712; (*n*) A. Corma, A. Leyva-Perez and M. J. Sabater, *Chem. Rev.*, 2011, **111**, 1657–1712; (*o*) D. Qian and J. Zhang, *Chem. Soc. Rev.*, 2015, **44**, 677–698; (*p*) R. J. Harris and R. A. Widenhoefer, *Chem. Soc. Rev.*, 2016, **45**, 4533–4551; (*q*) J. Xie, C. Pan, A. Abdukadera and C. Zhu, *Chem. Soc. Rev.*, 2014, **43**, 5245–5256; (*r*) T. C. Boorman and I. Larrosa, *Chem. Soc. Rev.*, 2011, **40**, 1910–1925; (*s*) M. Bandini, *Chem. Soc. Rev.*, 2011, **40**, 1358–1367; (*t*) V. Michelet, P. Y. Toullec and J.-P. Genêt, *Angew. Chem., Int. Ed.*, 2008, **47**, 4268–

4315; (*u*) A. S. K. Hashmi, *Chem. Rev.*, 2021, **121**, 8309–8310.

5 (*a*) A. Gómez-Suárez and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2012, **51**, 8156–8159; (*b*) T.-A. Nguyen, J. Roger, H. Nasrallah, V. Rampazzi, S. Fournier, H. Cattey, E. D. Sosa Carrizo, P. Fleurat-Lessard, C. H. Devillers, N. Pirio, D. Lucas and J.-C. Hierso, *Chem. – Asian J.*, 2020, **15**, 2879–2885; (*c*) V. R. Naina, F. Krätschmer and P. W. Roesky, *Chem. Commun.*, 2022, **58**, 5332–5346; (*d*) S. Witzel, A. S. K. Hashmi and J. Xie, *Chem. Rev.*, 2021, **121**, 8868–8925.

6 T.-A. Nguyen, E. Daiann Sosa Carrizo, H. Cattey, P. Fleurat-Lessard, J. Roger and J.-C. Hierso, Tetranuclear Dicationic Aurophilic Gold(I) Catalysts in Enyne Cycloisomerization: Cooperativity for a Dramatic Shift in Selectivity, *Chem. – Eur. J.*, 2022, e202200769.

7 V. Vreeken, D. L. J. Broere, A. C. H. Jans, M. Lankelma, J. N. H. Reek, M. A. Siegler and J. I. van der Vlugt, *Angew. Chem., Int. Ed.*, 2016, **55**, 10042–10046.

8 (*a*) E. S. Smirnova, J. M. Muñoz-Molina, A. Johnson, N. A. G. Bandeira, C. Bo and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2016, **55**, 7487–7491; (*b*) Already much simpler P,N-ligands have been shown to generate stable Au3 clusters: C. Khin, A. S. K. Hashmi and F. Rominger, *Eur. J. Inorg. Chem.*, 2010, 1063–1069.

9 (*a*) W. E. Brenzovich Jr., D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard III and F. D. Toste, *Angew. Chem., Int. Ed.*, 2010, **49**, 5519–5522; (*b*) E. Tkatchouk, N. P. Mankad, D. Benitez, W. A. Goddard and F. D. Toste, *J. Am. Chem. Soc.*, 2011, **133**, 14293–14300.

10 G. Zhang, L. Cui, Y. Wang and L. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 1474–1475.

11 (*a*) D. J. Faulkner, *Nat. Prod. Rep.*, 2001, **18**, 1–49; (*b*) S. Schulz and S. Hotling, *Nat. Prod. Rep.*, 2015, **32**, 1042–1066.

12 (*a*) M. E. Churchill, H. M. Sibhatu and C. L. Uhlson, *Methods Mol. Biol.*, 2011, **692**, 159–171; (*b*) M. I. Konaklieva and B. J. Plotkin, *Mini-Rev. Med. Chem.*, 2005, **5**, 73–95.

13 (*a*) E. F. Mohr, *Gold Chemistry, Applications and Future Directions in the Life Sciences*, Wiley-VCH, Weinheim, 2009; (*b*) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370–412.

14 P. Kumar, V. S. Kashid, Y. Reddi, J. T. Mague, R. B. Sunoj and M. S. Balakrishna, *Dalton Trans.*, 2015, **44**, 4167–4179.

15 (*a*) S. Bestgen, M. T. Gamer, S. Lebedkin, M. M. Kappes and P. W. Roesky, *Chem. – Eur. J.*, 2015, **21**, 601–614; (*b*) T. Tanase, R. Otaki, T. Nishida, H. Takenada, Y. Takemura, B. Kure, T. Nakajima, Y. Kitagawa and T. Tsubomura, *Chem. – Eur. J.*, 2014, **20**, 1577–1596; (*c*) T. P. Seifert, S. Bestgen, T. J. Feuerstein, S. Lebedkin, F. Krämer, C. Fengler, M. T. Gamer, M. M. Kappes and P. W. Roesky, *Dalton Trans.*, 2019, **48**, 15427–15434; (*d*) J. Ponce-de-León, R. Infante, M. Pérez-Iglesias and P. Espinet, *Inorg. Chem.*, 2020, **59**, 16599–16610.

16 D. V. Partyka, T. J. Robilotto, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2008, **27**, 28–32.

17 (*a*) M. Olaru, J. F. Kögel, R. Aoki, R. Sakamoto, H. Nishihara, E. Lork, S. Mebs, M. Vogt and J. Beckmann, *Chem. – Eur. J.*, 2020, **26**, 275–284; (*b*) D. Li, C.-M. Che, S.-M. Peng, S.-T. Liu, Z.-Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1993, 189–194; (*c*) A. J. Moro, B. Rome, E. Aguiló, J. Arcau, R. Puttreddy, K. Rissanen, J. C. Lima and L. Rodríguez, *Org. Biomol. Chem.*, 2015, **13**, 2026–2033; (*d*) A. Pinto, C. Roma-Rodrigues, J. S. Ward, R. Puttreddy, K. Rissanen, P. V. Baptista, A. R. Fernandes, J. C. Lima and L. Rodríguez, *Inorg. Chem.*, 2021, **60**, 18753–18763.

18 M. Dahlen, T. P. Seifert, S. Lebedkin, M. T. Gamer, M. M. Kappes and P. W. Roesky, *Chem. Commun.*, 2021, **57**, 13146–13149.

19 M. Saitoh, A. L. Balch, J. Yuasa and T. Kawai, *Inorg. Chem.*, 2010, **49**, 7129–7134.

20 (*a*) L. M. C. Luong, M. A. Malwitz, V. Moshayedi, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 2020, **142**, 5689–5701; (*b*) E. Aguiló, R. Gavara, C. Baucells, M. Guitart, J. C. Lima, J. Llorca and L. Rodríguez, *Dalton Trans.*, 2016, **45**, 7328–7339; (*c*) R. Gavara, A. Pinto, R. Donamaría, M. E. Olmos, J. M. López de Luzuriaga and L. Rodríguez, *Inorg. Chem.*, 2017, **56**, 11946–11955.

21 (*a*) T. Tanase, K. Masuda, J. Matsuo, M. Hamaguchi, R. A. Begum and S. Yano, *Inorg. Chim. Acta*, 2000, **299**, 91–99; (*b*) H. Xiao, Y.-X. Weng, W.-T. Wong, T. C. Mak and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1997, 221–226; (*c*) L. Rodríguez, M. Ferrer, R. Crehuet, J. Anglada and J. C. Lima, *Inorg. Chem.*, 2012, **51**, 7636–7641; (*d*) P. Baranyai, G. Marsi, C. Jobbágy, A. Domján, L. Oláh and A. Deák, *Dalton Trans.*, 2015, **44**, 13455–13459; (*e*) S. Nayeri, S. Jamali, A. Jamjah and H. Samouei, *Inorg. Chem.*, 2019, **58**, 12122–12131; (*f*) I. D. Strelnik, V. V. Sizov, V. V. Gurzhiy, A. S. Melnikov, I. E. Kolesnikov, E. I. Musina, A. A. Karasik and E. V. Grachova, *Inorg. Chem.*, 2020, **59**, 244–253.

22 J. R. Shakirova, E. V. Grachova, V. V. Sizov, G. L. Starova, I. O. Koshevoy, A. S. Melnikov, M. C. Gimeno, A. Laguna and S. P. Tunik, *Dalton Trans.*, 2017, **46**, 2516–2523.

23 I. O. Koshevoy, Y.-C. Chang, A. J. Karttunen, S. I. Selivanov, J. Janis, M. Haukka, T. Pakkanen, S. P. Tunik and P.-T. Chou, *Inorg. Chem.*, 2012, **51**, 7392–7403.

24 Z. Zhang and R. A. Widenhoefer, *Angew. Chem., Int. Ed.*, 2007, **46**, 283–285.

25 (*a*) R. L. Lalonde, B. D. Sherry, E. J. Kang and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 2452–2453; (*b*) Z. B. Zhang, C. F. Bender and R. A. Widenhoefer, *Org. Lett.*, 2007, **9**, 2887–2889; (*c*) Z. Zhang, C. F. Bender and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2007, **129**, 14148–14149; (*d*) R. L. LaLonde, Z. J. Wang, M. Mba, A. D. Lackner and F. D. Toste, *Angew. Chem., Int. Ed.*, 2010, **49**, 598–601.

26 O. Kanno, W. Kuriyama, Z. J. Wang and F. D. Toste, *Angew. Chem., Int. Ed.*, 2011, **50**, 9919–9922.

27 (*a*) L. Cui, G. Zhang and L. Zhang, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 3884–3887; (*b*) Y. Peng, L. Cui, G. Zhang and L. Zhang, *J. Am. Chem. Soc.*, 2009, **131**, 5062–5063.

28 (*a*) A. S. K. Hashmi, T. D. Ramamurthi and F. Rominger, *J. Organomet. Chem.*, 2009, **694**, 592–597; (*b*) A. S. K. Hashmi, T. D. Ramamurthi, M. H. Todd, A. S.-K. Tsang and K. Graf, *Aust. J. Chem.*, 2010, **63**, 1619–1626.

29 Phenylboronic acid was purified prior to use following the protocol described in the literature: R. K. Arvela, N. E. Leadbeater, M. S. Sangi, V. A. Williams, P. Granados and R. D. Singer, *J. Org. Chem.*, 2005, **70**, 161–168.