

Base-assisted synthesis of 4-pyridinate gold(I)metallaligands; study of their use in Self-Assembly reactions.

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Abstract

The synthesis of di- and tritopic gold(I) metallaligands of the type [(Au₄-py)₂(μ₂-diphosphane)] (diphosphane = bis(diphenylphosphanyl)isopropane or dppip (**1**), 1,2-bis(diphenylphosphanyl)ethane or dppe (**2**), 1,3-bis(diphenylphosphanyl)propane or dppp (**3**), 1,4-bis(diphenylphosphanyl)butane or dppb (**4**)), and [(Au₄-py)₃(μ₃-triphosphane)] (triphosphane = 1,1,1-tris(diphenylphosphanylmethyl)ethane or triphos (**5**) and 1,3,5-tris(diphenylphosphanyl)benzene or triphosph (**6**)) from [(AuCl)₂(μ₂-diphosphane)] or [(AuCl)₃(μ₃-triphosphane)] and 4-pyridylboronic acid in the presence of Cs₂CO₃ has been conducted. Interestingly, when [(AuCl)₂(μ₂-dppm)] (dppm = bis(diphenylphosphanyl)methane) was used as a starting material the cyclic tetranuclear gold(I) compound [(Au₄-py)₂(CH)₂(μ₂-Au(PPh₂)₂)] (**I**), was obtained instead. All the products have been characterized by IR and multinuclear NMR spectroscopies, mass spectrometry and elemental analysis and in the case of **1**, **3**, **5** and **I** by X-ray crystallography, which showed the presence of aurophilic interactions in all of them. The obtained metallaligands have been used as building blocks in self-assembly reactions with *cis*-blocked palladium or platinum acceptor moieties producing [2+2] metallamacrocycles or trigonal bipyramidal (TBP) [2+3]

metallaligands in good yields. The photophysical properties of both the metallaligands and the corresponding assemblies have been investigated.

Introduction

The use of organometallic gold(I) complexes as building blocks has become a very useful strategy for the assembly of different species with specific structures such as macrocycles, helicates, cages, catenanes, rigid-rod oligomers or polymers among others.¹ Both the linear coordination and the tendency to establish aurophilic interactions between gold centers² are the two main factors for the use of gold(I) complexes in the formation of supramolecular structures by self-assembly that often display interesting photoluminescence from metal- and/or ligand-based excited states.

Pyridine is one of the most versatile ligands in coordination chemistry; it forms stable complexes with most transition metal cations and has been used as a donor fragment in the coordination-driven self-assembly of a wealth of architectures.³ The fact that gold(I) prefers phosphorus, sulfur or carbon donor ligands due to its soft character opens the possibility of designing gold(I) metallaligands containing dangling pyridine rings appropriate to coordinate with other transition metal moieties in self-assembly reactions. Effectively, several classes of gold(I) metallaligands bearing terminal pyridine rings as a appended unit of other P-, S- or C-bonded fragments have been described, including pyridine phosphanes,⁴ pyridine thiolates,⁵ pyridine carbenes,⁶ pyridine acetylenes,⁷ and tetrafluorobenzene-pyridine⁸ (Chart 1). Many of them have been successfully used as building blocks in the formation of a wide range of supramolecular assemblies, as it has been recently comprehensively reviewed.^{1b}

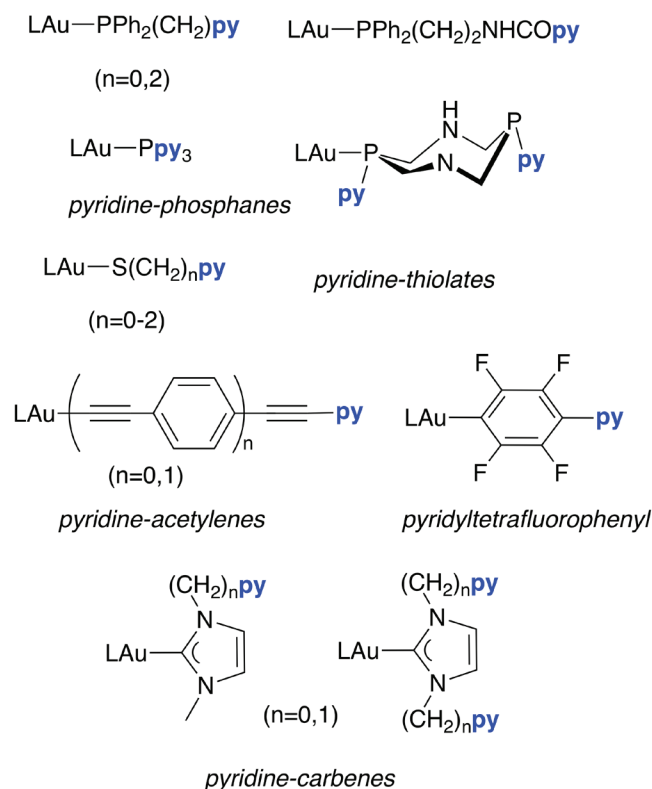


Chart 1

With the exception of the mononuclear compounds $\text{Cy}_3\text{PAu}(4\text{-py})$ (PCy_3 = tricyclohexylphosphane),⁹ $\text{JohnPhosAu}(3\text{-py})$ (JohnPhos = $\text{di}(\text{tert-butyl})(1,1'\text{-biphenyl-2-yl})\text{phosphane}$ and $\text{'BuXPhosAu}(3\text{-py})$ ('BuXPhos = $\text{di}(\text{tert-butyl})(2',4',6'\text{-triiisopropylbiphenyl-2-yl})\text{phosphane}$)¹⁰ none of the reported pyridine-containing metallaligands presents a direct bond between the pyridine ring and the gold(I) center, most probably due to synthetic difficulties. Arylgold(I) complexes have historically been synthesized by the reaction of a gold (I) halide with an aryl-lithium prepared in situ.¹¹ Often, the use of organolithium reagents gives rise to reduction processes that result in very low yields and rather experimentally demanding procedures. Gold-carbon bond formation from boronated precursors has emerged as a general and functionally tolerant alternative way of synthesizing gold(I) organometallics; product formation proceeds neatly in high to moderate yields, regardless of the nature of the other ligands.¹²

Our earlier work dealing with the synthesis and study of self-assembly reactions of gold(I) compounds that combines both di- tri or tetraphosphanes and ethynylpyridine^{7b} or tetrafluorobenzenepyridine¹³ units has shown that the nature of resulting assemblies depends not only on the length and flexibility of the metallaligand, but also on the group directly

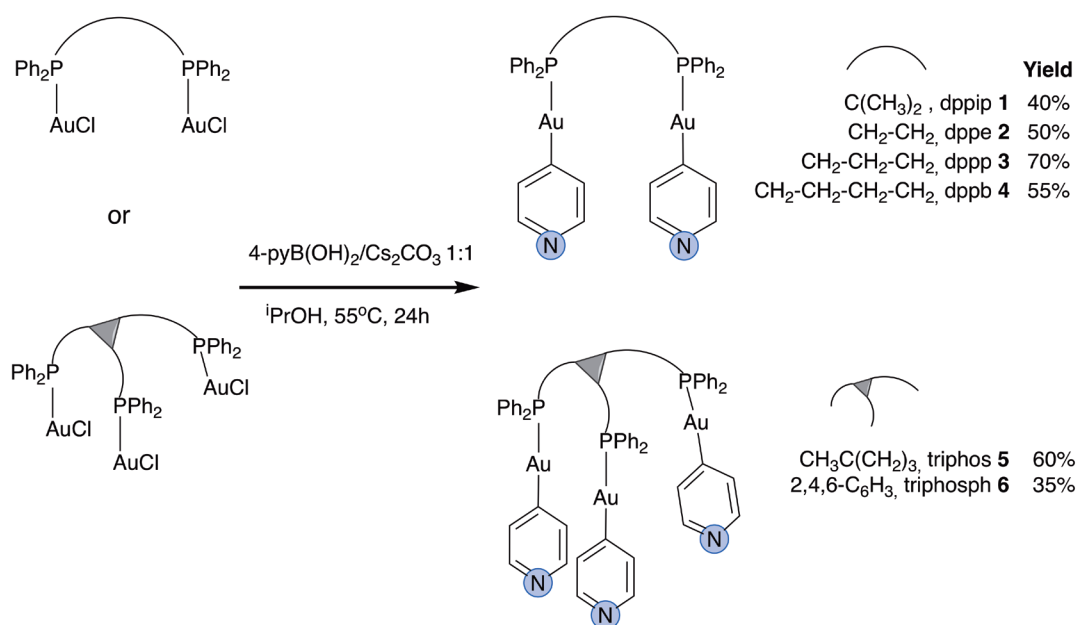
bonded to the pyridine ring. In fact, although both metallamacrocycles of diverse nuclearity¹³ and cages¹⁴ were isolated, only uncharacterizable mixtures of polynuclear species were obtained in some instances.^{7c} In addition, the presence of gold(I) also allowed us to investigate the photophysical properties of some of these compounds, and thus try to establish structure-properties relationships.^{7b, 15}

In order to expand our previous findings in the field we are here reporting the synthesis of di and tritopic polyphosphane containing organometallic Au(I) metallaligands, where the metal center is attached directly to the pyridine donor fragment. Furthermore, the study of the participation of these compounds in self-assembly processes with square planar species of palladium and platinum is also investigated. Finally, the photophysical properties of the obtained compounds have been investigated in order to find differences in the absorption and emission properties between the free metallaligands and when included in the assembled aggregates.

Results and Discussion

Synthesis of di and tritopic 4-pyridinate gold(I) metallaligands

Following the reported base-assisted transmetallation from boronic-acids procedure,^{12, 16} the organogold(I) di- and triphosphane complexes $[(Au4-py)_2(\mu_2-diphosphane)]$ (diphosphane = dppip (**1**), dppe (**2**), dppp (**3**), dppb (**4**)), and $[(Au4-py)_3(\mu_3-triphosphane)]$ (triphosphane = triphos (**5**) and triphosph (**6**)) were prepared in moderate to good yields from $[(AuCl)_2(\mu_2-diphosphane)]$ or $[(AuCl)_3(\mu_3-triphosphane)]$ (alternatively, the use of analogous bromido derivatives gave similar yields) and a large excess of 4-pyridylboronic acid in isopropanol at 55°C; the reaction mixture is kept in the dark in the presence of the same number of moles of Cs_2CO_3 as a base (Scheme1). The molar ratio between the chlorido compounds and the 4-pyridylboronic acid resulted to be highly dependent on the phosphane ligand. While good yields of the dppip (**1**) and dppp (**3**) compounds were obtained using an optimal 1:4 ratio of $[(AuCl)_2(\mu_2-diphosphane)]: 4-pyB(OH)_2$, this molar ratio had to be raised to 1:6 and 1:10 for dppe (**2**) and dppb (**4**) derivatives, respectively. For the triphosphane derivatives, a $[(AuCl)_3(\mu_3-triphosphane)]: 4-pyB(OH)_2$ 1:6 molar ratio produced the tritopic ligands **5** and **6** in moderate yields.



Scheme 1. Synthesis of the 4-pyridinate gold(I) metallaligands

All the synthesized compounds were characterized by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy, high-resolution mass spectrometry (ESI+), IR spectroscopy and elemental analysis. In addition, the structures of **2**, **3** and **5** were determined by X-ray crystallography (see below).

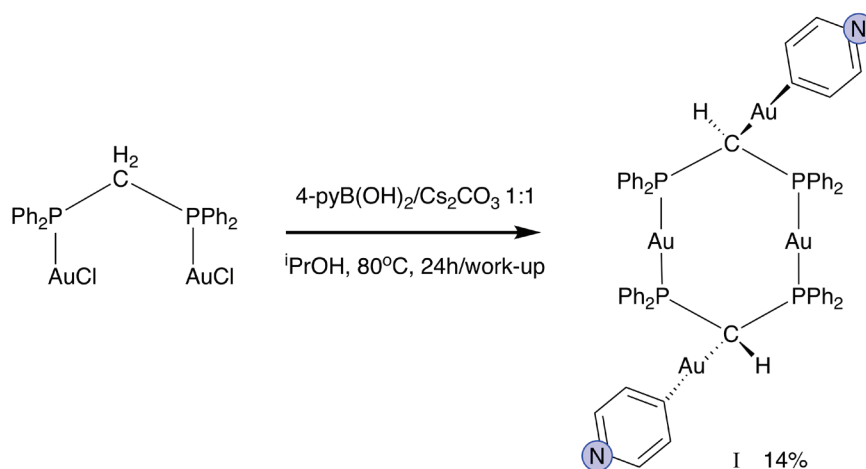
As expected by the chemical equivalence of the phosphorus atoms, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show only one signal whose chemical shift appears slightly downfield shifted (5-10 ppm) with respect to that of the initial chlorido complexes. The ^1H NMR spectra show the signals due to both α and β protons of the pyridine rings and those attributable to the phosphane ligands.

High resolution mass spectra (ESI+) display peaks corresponding to $[\text{M}+\text{H}]^+$ and $[\text{M}+2\text{H}]^{2+}$ (for ditopic **1-4**) and $[\text{M}+3\text{H}]^{3+}$ (for tritopic **5** and **6**) as a result of the protonation of all the terminal pyridine groups.

Reaction with dppm

In contrast with the phosphanes described above, when the dppm derivative $[(\text{AuCl})_2(\mu_2\text{-dppm})]$ was treated with 4-pyridylboronic acid and Cs_2CO_3 in isopropanol under the aforementioned conditions, a complex mixture of compounds was obtained (as observed in both the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra). After scanning new reaction conditions, we found that an increase in temperature gave rise to a mixture where a main product could be observed. After workup, the new tetranuclear $[(\text{Au}4\text{-py})_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$ (**I**) compound, where each methylene group in the dppm is singly deprotonate and coordinate to a Au(I)-

pyridine moiety, was serendipitously isolated but in a very low yield. (Scheme 2) Unfortunately, despite numerous efforts trying to improve the reaction conditions, we were not able to obtain a better yield of the named tetragold compound.



Scheme 2. Synthesis of the tetranuclear dppm derivative (**I**)

So the base-assisted transmetalation, although generally reliable, can be inefficient for Brønsted acidic substrates (as reported by other groups),⁹ precluding the obtention of the targeted compounds. In our case, the acidity of the methylene protons in the carbon chain of dppm seems to be the responsible of the unexpected alternative reaction.

Alternatively, a more rational route was explored starting from the preformed tetranuclear $[(\text{AuCl})_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$.¹⁷ We attempted to introduce in the latter the 4-pyridine fragment by a base-assisted transmetalation with 4-pyridylboronic acid or by the classical reaction with 4-pyridyllithium. Again, the resulting reactions were not clean and the desired product was only obtained in a very low yield. This fact effectively ruled out the study of the participation of the compound $[(\text{Au}4\text{-py})_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$ (**I**) as a ditopic metallaligand in self-assembly processes, despite its interest as a tetragold building block.

Compound **I** was completely characterized in solution by multinuclear (^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$) and bidimensional (^1H - ^1H COSY, ^1H - ^{13}C HSQC) NMR, and HRMS-ESI(+) spectrometry (see S19- S24 in Supporting information). As expected, the $^{31}\text{P}\{^1\text{H}\}$ NMR presents only one peak, whose chemical shift (34.6 ppm) is very similar to those described for the analogous $[\text{Au}_2(\text{acac})_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$,¹⁸ $[\text{Au}_2(\text{C}_6\text{F}_5)_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$ ¹⁹ and $[\text{Au}_2\{(\text{PBr}(\text{CO}_3)(\text{NO}_3))_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$ (HPB = 2-(2'-pyridyl)benzimidazole).²⁰ The occurrence in the ^1H NMR spectrum of a pseudoquintuplet at 3.17 ppm ($J(\text{H-P}) = 3.5$ Hz), due to the virtual coupling of the chemically but not magnetically equivalent phosphorus atoms

with the methylene protons, is indicative of a large $J_{\text{trans}}(^{31}\text{P}-^{31}\text{P})$ in addition to the likely existence of intramolecular aurophilic contacts in solution.^{7b,21} In fact, a Au··Au contact of 2.9763(3) Å is present in the molecular structure of the compound determined by X-ray crystallography in solid state. (see below).

X-ray crystallography

Crystals of compounds **2**, **3** and **5** suitable for X-ray diffraction studies were obtained from slow diffusion of diethylether into dichloromethane solutions and their molecular structures are shown in Figure 1; crystal data can be found in Supporting Information. Some of the most relevant features of the determined structures are indicated below.

Compound **2** displays a *cis* disposition of the diphosphane (Au1-P1-P1a-Au1a = 48°), thus allowing the establishment of intramolecular Au··Au interactions (3.1887(4) Å). This arrangement contrasts with the *trans* conformation found for dppe in the closely related complexes [(AuFMes)₂(μ₂-dppe)]²² and [(AuMes)₂(μ₂-dppe)]²³ where no interactions Au··Au are detected.

Similarly, compound **3** shows a *cis* conformation for dppp (torsion angle Au1-P1-P1a-Au1a = 71°), again favouring the establishment of aurophilic interactions (d(Au··Au)= 3.1581(2) Å). An analogous arrangement is found in the X-ray structure of the related compound [(Au4-F-C₆H₄)₂(μ₂-dppp)]²⁴ (d(Au··Au)= 2.997 Å, Au1-P1-P1a-Au1a = -57°).

In the crystal lattice, compound **3** forms rows of molecules following the *b*-axis, where C-H··π(ring) weak interactions between hydrogen atoms of the alkyl chain of the dppp and the pyridine rings of adjacent molecules can be observed (see Figure S48).

The molecular structure of compound **5** (Figure 1) features the association of the trinuclear derivatives into dimers, so that all the gold(I) atoms are involved in aurophilic interactions, (Figure S49) with an intramolecular Au1...Au2 distance (3.2044(14) Å) that is larger than the intermolecular one ($d(\text{Au3}\cdots\text{Au3}') = 3.1717(17)$ Å). The C_2 symmetry of the dimers (C_2 axis passing through the middle point of Au3...Au3' intermolecular bond) makes them chiral and a racemic mixture is found in the crystal. This arrangement differs from that exhibited by other organometallic compounds of gold(I) that contain 1,1,1-tris(diphenylphosphinomethyl),^{7b, 8, 25} where a pair of branches of the triphosphane are near enough to allow aurophilic contacts while the third one lies far apart. An analysis of the molecular packing reveals that each of the dimers participates in four weak C-H...N_{py} interactions (2.62 Å), producing a 3D organization of the compound (Figure S50).

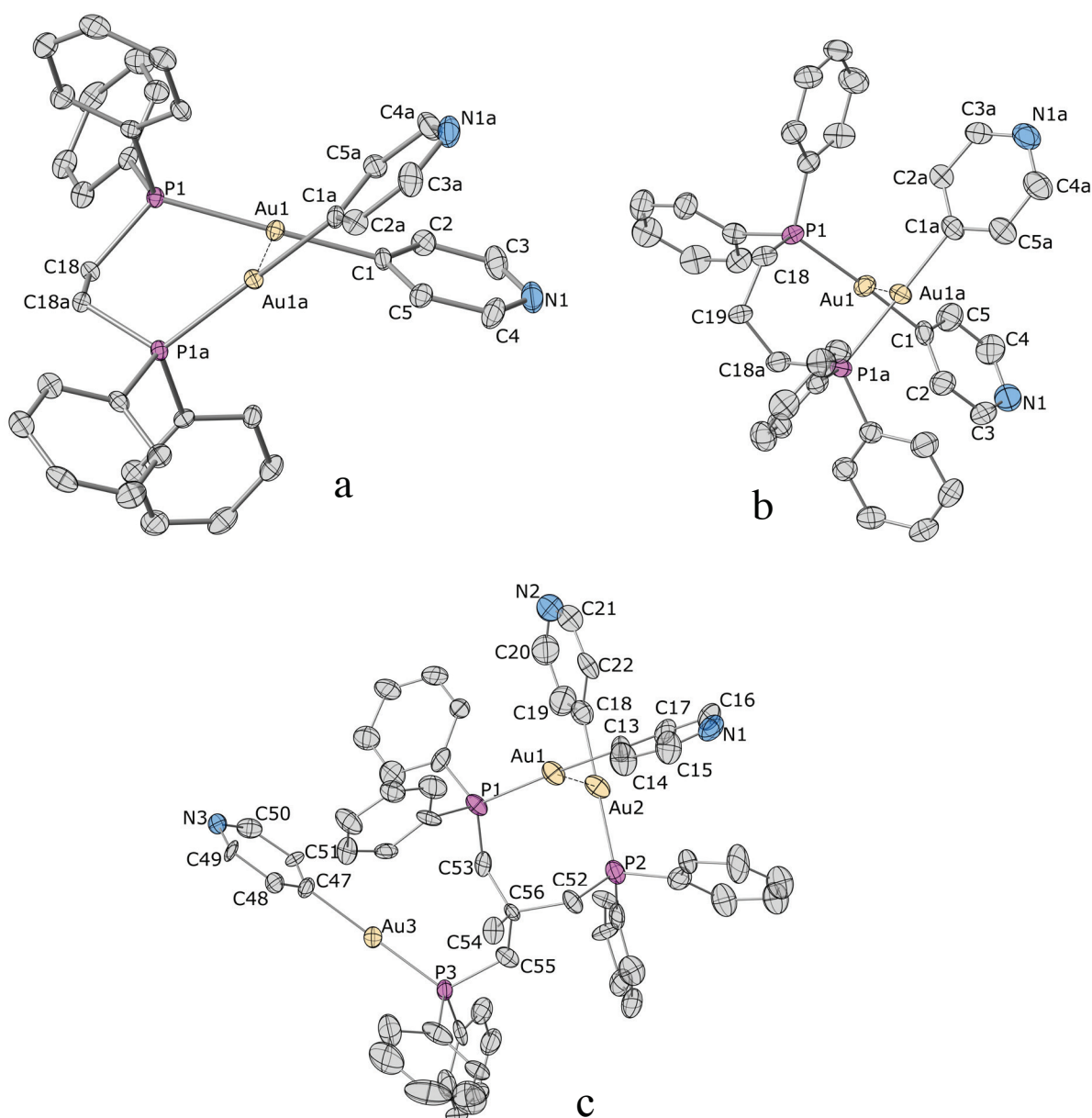


Figure 1. Molecular structures of compounds (a)[(Au4-py)₂(μ₂-dppe)] (**2**), (b)[(Au4-py)₂(μ₂-dppp)] (**3**) and (c)[(Au4-py)₃(μ₃-triphos)] (**5**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are indicated in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2**, **3**, **5** and **I**

Compound 2			
Au1...Au1a	3.1887(4)	P1-Au1-C1	174.84(15)
Au1-P1	2.2951(13)	P1-C18-C18a	117.1(3)
Au1-C1	2.063(5)	P1-Au1-Au1a	87.78(3)
P1-C18	1.831(5)	C1-Au1-Au1a	97.30(15)
Compound 3			
Au1...Au1b	3.1581(2)	P1-Au1-C1	174.58(9)
Au1-P1	2.3052(7)	P1-C18-C19	114.9(2)
Au1-C1	2.052(3)	P1-Au1-Au1a	83.936(18)
P1-C18	1.826(3)	C1-Au1-Au1a	101.11(9)
		C18-C19-C18a	117.8(4)
Compound 5			
Au1...Au2	3.2044(14)	P1-Au1-C13	173.1(9)
Au1-P1	2.290(6)	P1-C53-C56	119.9(16)
Au1-C13	2.08(2)	C53-P1-Au1	115.3(8)
P1-C53	1.83(3)	P1-Au1-Au2	84.54(16)
Au2-P2	2.290(8)	C13-Au1-Au2	101.2(7)
Au2-C18	2.02(3)	P2-Au2-C18	177.4(8)
P2-C52	1.84(2)	P2-C52-C56	123.7(16)
Au3-P3	2.295(6)	C52-P2-Au2	116.1(10)
Au3-C47	2.12(2)	P2-Au1-Au2	86.77(18)
P3-C55	1.82(3)	C18-Au2-Au1	95.7(8)
		P3-Au3-C47	174.4(6)
		P3-C55-C56	121.0(18)
		C55-P3-Au3	116.8(10)
		C54-C56-C52	104.6(18)
		C54-C56-C53	115(2)

		C54-C56-C55	110(2)
Compound I			
Au3...Au4	2.9763(3)	P2-Au3-P3	175.96(4)
Au3-P2	2.3106(11)	P1-Au4-P4	177.49(4)
Au3-P3	2.3082(11)	P2-Au3-Au4	87.80(3)
Au4-P1	2.3108(11)	P1-Au4-Au3	92.34(3)
Au4-P4	2.3104(11)	P4-Au4-Au3	87.12(3)
Au1-C1	2.025(5)	P3-Au3-Au4	92.54(3)
Au1-C30	2.137(5)	C1-Au1-C30	176.41(19)
Au2-C31	2.030(5)	C31-Au2-C60	175.31(19)
Au2-C60	2.141(5)	Au1-C30-P1	99.1(2)
P1-C30	1.790(5)	Au1-C30-P2	105.5(2)
P2-C30	1.793(5)	Au2-C60-P3	102.1(2)
P3-C60	1.792(5)	Au2-C60-P4	103.4(2)
P4-C60	1.788(5)	P1-C60-P2	112.7(3)
		P3-C60-P4	112.0(3)

The molecular structure of compound **I** was also established by single-crystal X-ray diffraction (Crystal Data can be found in Supporting Information). The crystal lattice is composed of cyclic [(Au4-py)₂(CH)₂(μ₂-Au(PPh₂)₂)] molecules with the eight-membered Au₂P₄C₂ ring in a chair conformation (Figure 2) and dichloromethane solvent molecules. According with the general trend observed in other compounds containing this type of structure,^{18-20, 26} there is a short intramolecular Au...Au contact (2.9763(3) Å) whose value is very similar to that found in the closely related [(AuL)₂(CH)₂(μ₂-Au(PPh₂)₂)] (L = acac 2.969 Å,¹⁸ C₆F₅ 2.917 Å¹⁹ and {(PRe(CO)₃(NO₃)₂)} 2.982 Å.²⁰ Both the methylene protons of dpmm and the nitrogen atoms of the pyridine groups are again involved in weak C-H...N_{py} interactions (2.45-2.50 Å) giving rise to a 2D layer structure disposed in a parallel way to the ac plane of the crystal packing (Figure S51).

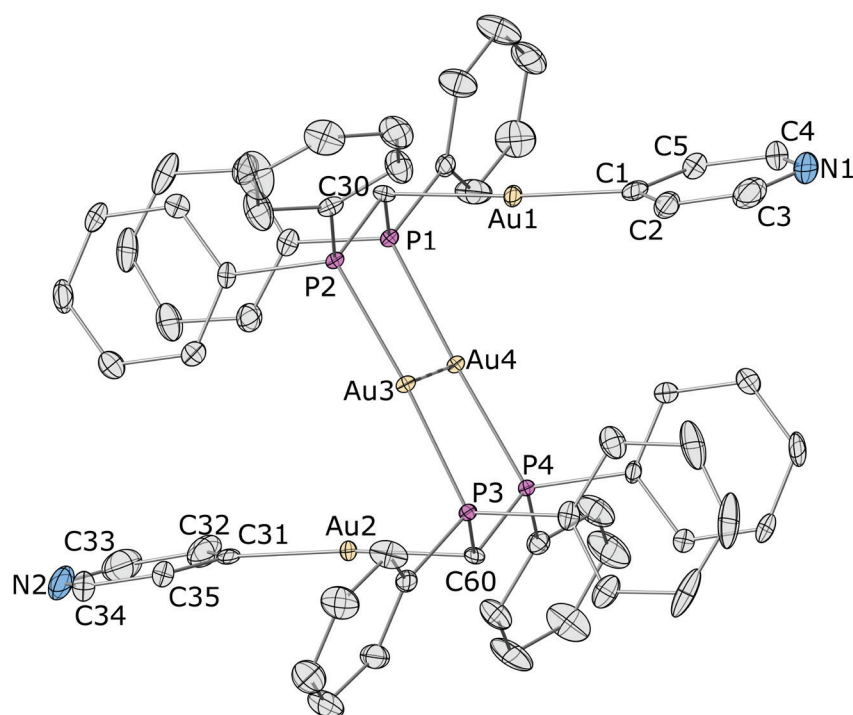


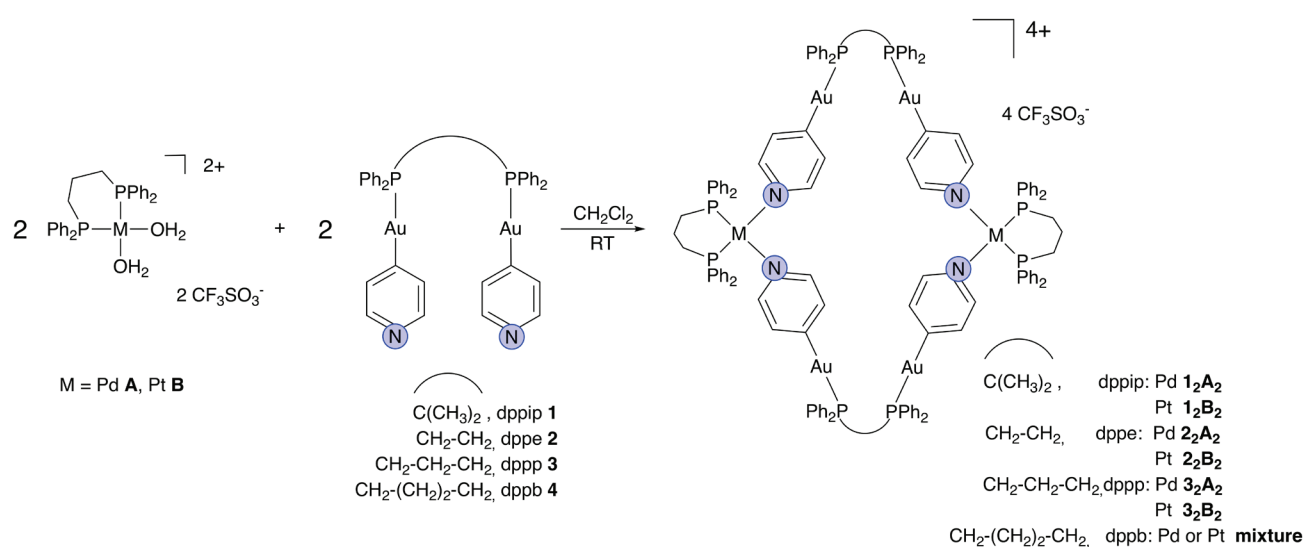
Figure 2. Molecular structure of the compound $[(\text{Au}_4\text{-py})_2(\text{CH})_2(\mu_2\text{-Au}(\text{PPh}_2)_2)]$ (**I**) Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are indicated in Table 1.

Self-assembly studies

In our previous studies where the tetrafluorobenzenepyridine ditopic metallaligands $[(\text{AuC}_6\text{F}_4\text{-py})_2(\mu_2\text{-diphosphane})]$ were reacted with the acceptor square-planar $[\text{M}(\text{dppp})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ compounds, we observed the preferred formation of [2+2] assemblies (two donor + two acceptor building-blocks) over higher nuclearity species [3+3] or [4+4].¹³ No correlation between the length and/or flexibility of the metallaligands was inferred from the formation of small quantities of high nuclearity species in equilibrium with the main [2+2] aggregates in some cases. On the other hand, the formation of discrete assemblies was not observed when the related alkynyl metallaligands $[(\text{AuC}\equiv\text{C}_4\text{-py})_2(\mu_2\text{-diphosphane})]$ were used in the same sort of processes.^{7b} These results prompted us to investigate the nature of the species obtained in the self-assembly reactions between the smaller gold(I) ditopic metallaligands described in this work and the *cis*-blocked square-planar palladium or platinum compounds indicated above.

Thus, square-planar acceptor compounds $[\text{M}(\text{dppp})(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_2$ ($\text{M} = \text{Pd}$ **A**, Pt **B**) were treated with the ditopic donors $[(\text{Au}_4\text{-py})_2(\mu_2\text{-diphosphane})]$ [diphosphane = dppip (**1**), dppe (**2**) dppp (**3**), and dppb (**4**)] in 1:1 molar ratio in dichloromethane solution at room temperature (Scheme 3). After 1 hour of stirring, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction

solutions (except in the case of **4**) showed two distinct resonances, in agreement with the formation a single discrete symmetrical assembly containing two sets of chemically non-equivalent phosphorus atoms *i.e.* P-Au and P-M (Pd, Pt). Analogously to that reported for the tetrafluorobenzene derivatives, the phosphorus nuclei corresponding to the acceptor fragment appear upfield shifted (*ca.* 5 ppm) while the signals of the diphosphane attached to gold(I) centers barely undergo any chemical shift change after the self-assembly process. More informative is the value of $^1J(^{31}\text{P}-^{195}\text{Pt})$ in the platinum assemblies. Its decrease of approximately 700 Hz by comparison with that of $[\text{Pt}(\text{dppp})(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_2$ is an evidence of the coordination of pyridine-ended metallaligands to the acceptor complexes.



Scheme 3. Self-assembly of [2+2] metallamacrocycles

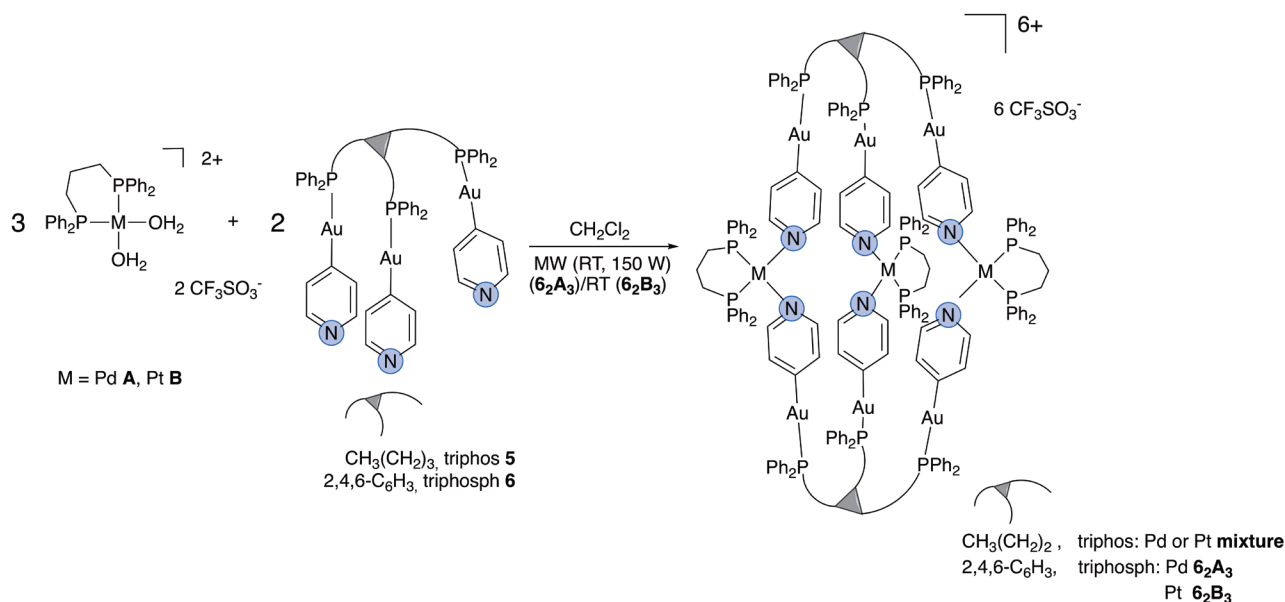
As indicated above, the most insoluble $[(\text{Au}4\text{-py})_2(\mu_2\text{-dppb})]$ (**4**) did not produce the selective formation of discrete aggregates as indicated by the complex $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction solutions. The insolubility of compound **4** could be due to the formation of polymeric species that preclude the pyridine coordination to the acceptor compounds.

After the adequate workup, the desired metallamacrocycles could be isolated as solids and characterized. Interestingly, the ^1H NMR spectra do not show the expected downfield shift of α -pyridine protons, characteristic of the coordination of pyridine rings to metal centers.¹³ This is most probably due to the fact that the deshielding associated to electron donation opposes with the upfield shift due to the anisotropic effect exerted by the phenyl rings of the dppp ligands attached to either palladium or platinum centers in the assembly. In parallel, a

significant upfield shift was observed for the β -pyridine protons (≈ 0.5 ppm), in agreement with the influence of the ring currents of the close phenyl rings.

High resolution ESI(+)-MS spectrometry allowed to establish the stoichiometry of the self-assembled species. As can be seen in the Supporting Information Section, all the studied metallamacrocycles present peak series that are in agreement with the exclusive formation of [2+2] architectures. For most of the compounds, several charged aggregates are obtained by subsequent loss of triflate anions, being their isotopic distribution in agreement with the theoretical one.

To explore the possibility of obtaining more complex architectures, such as metallacages, as those that have been selectively built by combination of tripodal ligands and cis-blocked Pd^{II} or Pt^{II} square-planar complexes,²⁷ the self-assembly reaction between the tritopic gold(I) metallaligands [(AuC₆F₄4-py)₃(μ_3 -triphosphane)] (triphos **(5)**, triphosph **(6)**) and [M(dppp)(H₂O)₂](CF₃SO₃)₂ was investigated. For the more flexible triphos derivative **(5)**, only complex ³¹P{¹H} NMR patterns were obtained from the reaction solutions, indicating that the expected metallacages were not assembled. Nevertheless, the analogous reaction of compound [(AuC₆F₄4-py)₂(μ_3 -triphosph)] **(6)** with the acceptor palladium or platinum square-planar compounds **A** and **B** did effectively produce the new [2+3] TBP cages (**6₂A₃**) and (**6₂B₃**) as a result of the assembly of two tripodal ligands and three M(dppp) units (Scheme 4).



Scheme 4. Self-assembly of TBP [2+3] cages.

Although the formation of the platinum-gold cage (**6₂B₃**) takes place neatly in CH₂Cl₂ at room temperature within 60 minutes of reaction, the selective assembly of the analogous palladium-gold cage (**6₂A₃**) necessitates microwave irradiation in isopropanol (150W, 25 °C) to avoid the formation of a mixture of compounds when the platinum-gold cage reaction conditions are used. The identity and purity of the cages were proven by ¹H and ³¹P{¹H} NMR spectroscopy and ESI-MS spectrometry. ³¹P{¹H} NMR spectra show two sharp singlets, which are consistent with the existence of two groups of chemically equivalent phosphorus atoms (Au-P and Pd-P or Pt-P) (see Fig. S44 and S47, respectively). Unlike the [2+2] species, the ¹H NMR spectroscopic comparison of **6** and **6₂A₃** or **6₂B₃** shows the expected downfield shift of the α-pyridine upon coordination to metal centers. Particularly informative are the ESI-MS spectra that confirm the [2+3] composition of the assemblies. A major set of peaks with +2, +3 and +4 charge are observed (due to the subsequent loss of CF₃SO₃⁻), with the experimental isotope patterns of m/z for each charge state consistent with the corresponding calculated values (see Figure S45 for **6₂A₃** and Figure 3 for **6₂B₃**). To our knowledge, compounds **6₂A₃** or **6₂B₃** are the first examples of heterometallic palladium or platinum cages containing gold(I) centres. Although we have not been able to isolate a crystal suitable for X-ray analyses, Spartan calculations²⁸ were undertaken in order to optimise the proposed BPT structure of the synthesized cages. A representation of the minimized structure of the cationic part of compound **6₂A₃** is depicted in the Supporting Information (Fig. S52).

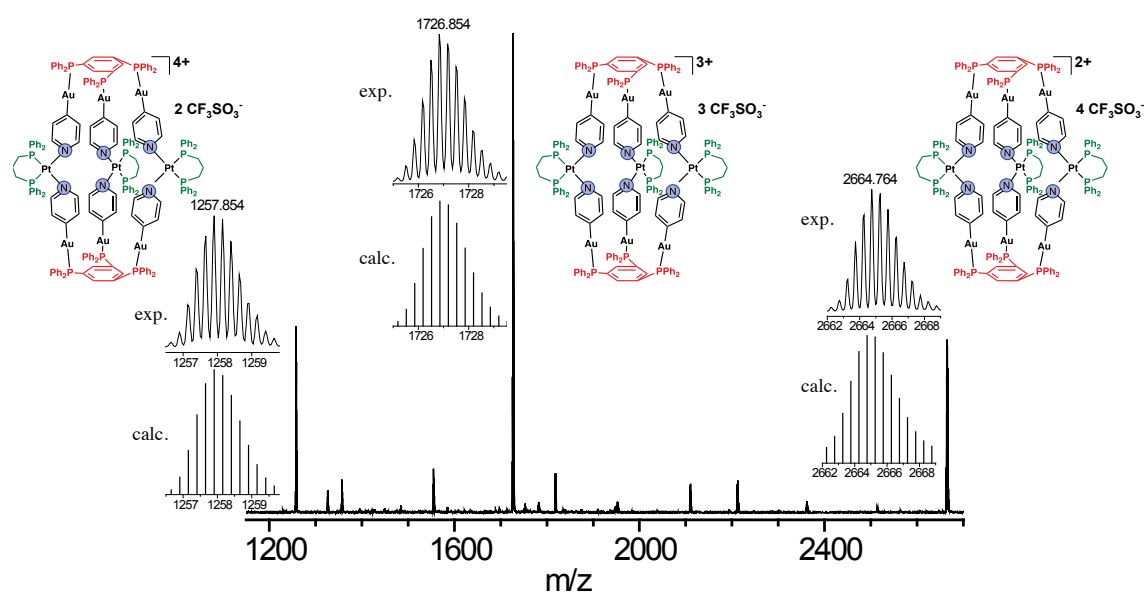


Figure 3. ESI(+)-HRMS spectrum of $[\{(Au4-py)_3(\mu_3\text{-triphosph})\}_2\{Pt(dppp)\}_3](CF_3SO_3)_6$ (**6₂B₃**) in $CDCl_3$ at 298 K. The insets show the experimental(top) and calculated(bottom) isotope patterns for the $[M-2CF_3SO_3]^{2+}$, $[M-3CF_3SO_3]^{3+}$ and $[M-4CF_3SO_3]^{4+}$ species.

Photophysical Studies

Absorption and emission spectra of all the compounds were recorded in dichloromethane solution at room temperature; the obtained data are listed in table 2.

Table 2. Absorption and emission maxima, quantum yields and lifetimes of the obtained compounds measured in dichloromethane solution at room temperature. * the very low solubility of the compound precluded the determination of ϵ .

Compound	Absorption λ_{max} , nm ($10^{-3} \times \epsilon$, $M^{-1}cm^{-1}$)	Emission λ_{max} , nm	Quantum yield, ϕ	Lifetime τ , ns
1	265sh (14), 311 (5.6)	374	0.005	2.5
2	266sh (12), 274sh (9.3), 309 (4.5)	373	0.007	2.2
3	274sh (14), 293 (9.1)	372	0.007	2.4
4	265sh, 274sh, 291*	366	0.004	2.6
5	267sh (16), 275sh (12), 300sh (6.7)	372	0.005	2.9
6	277sh (15), 295sh (6.9)	367	0.005	2.5
I	300 (28)	375	0.007	3.2
1₂A₂	265sh (56), 273 (52)	378	0.005	4.7
1₂B₂	277sh (24), 331 (9.6)	376	0.006	4.8
2₂A₂	266sh (7.1), 275sh (63)	370	0.004	2.3
2₂B₂	275sh (59), 315 (25)	373	0.004	2.0
3₂A₂	267sh (67), 275sh (60)	372	0.004	2.5
3₂B₂	274sh (16), 305 (5.9)	372	0.004	2.6
6₂A₃	260sh (146), 275(130)	378	0.003	2.8
6₂B₃	275sh (58), 290 (28)	370	0.004	2.4

The UV-vis spectra of the gold(I) compounds **1-6** in CH_2Cl_2 solution (Figure S53 above) show two different regions. The higher energy region (265-275 nm) contains intense poorly

resolved absorption bands, which are characteristic of allowed IL phosphane transitions,^{12b, 29} while the less intense and more defined band at *ca.* 300 nm could be assigned to a IL and/or metal- perturbed IL transitions; nevertheless, a contribution of weak-gold-gold interactions could not be discarded.^{21, 29b} In fact compound **I**, which presents the closest Au...Au contact (see above) shows an intense and well-defined band at 300 nm that has been assigned to a IL transitions perturbed by intramolecular Au-Au interactions in related compounds.³⁰

These bands are not significantly affected by the coordination to either the palladium or the platinum moieties. As expected, higher molar extinction coefficients are observed in the case of metallamacrocycles (Figure S54) where two slightly different absorption profiles can be found. While palladium species display shoulders (260-275 nm) similar to those of parent metallaligands with tails extending to 350 nm, platinum compounds present, a rather defined band at lower energies.

Excitation of the dichloromethane solution of all the compounds at the lowest energy absorption band produces a weak broad emission band in the 360-380 nm range (Figure S53 and S54), being the emission wavelengths of both the metallaligands and the corresponding heterometallic assemblies almost identical. Similar values of the emission quantum yields for all the analyzed species are recorded. The small Stokes' shift and the broad shape of all the obtained bands, as well as the fact that lifetimes are in the order of nanoseconds, let us assign the resulting emissions to a metal-perturbed ¹IL fluorescence transitions involving phenyl and probably pyridyl rings. In this respect, the emission maxima of the compounds studied in this work closely resemble those of the chlorido [(AuCl)_n(μ_n-phosphane)] precursors.^{31,32} As a whole, the experimental data is in agreement with the fact that the observed emission raises from the gold metallaligands and the formation of the metallamacrocycles does not affect significantly the luminescent properties of the former.

Conclusions

Herein, we have reported the use of base-assisted transmetallation reaction for the facile and high yielding syntheses of a series of di- and tritopic gold(I) metallaligands with terminal 4-pyridyl groups. The X-ray structural determination of the synthesized compounds revealed that the establishment of aurophilic interactions strongly determines the spatial arrangement within the molecules in the different species.

The base-assisted transmetallation has been proved to fail for the dpmm derivative due to the Bronsted acidity of the methylene protons of the carbon chain. In this particular case, the

cyclic tetranuclear $[(Au_4-py)_2(CH)_2(\mu_2-Au(PPh_2)_2)]$ (**I**) compound has been obtained through an unknown mechanism of reorganization.

Reactions of the obtained new gold(I) organometallic donor species with Pd or Pt square-planar acceptor complexes afford, in most of the cases, the formation of [2+2] metallamacrocycles or TBP [2+3] metallacages in a selective way, which is in deep contrast with previously reported results obtained with metallaligands with longer dangling pyridine-ended arms.

Photophysical characterization reveals the presence of very similar in energy and shape metal-perturbed ¹IL weak emission bands for all the synthesized compounds. This fact together with the close values of quantum yields recorded for all the species are a clear indication that the inclusion of the metalloligands in the polymetallic macrocycles or cages has not any influence on their luminescence properties.

In addition to their synthesis and characterization, it is important to remark that the supramolecules reported here form cavities of different shape/and size that can interact with different compounds and give rise to a change in their photophysical properties. Ongoing work is focusing on the obtention of new emissive gold(I) self-assembled architectures and the study of their participation in molecular recognition processes.

Experimental Section

General Methods.

All manipulations were performed under prepurified nitrogen atmosphere using Schlenck-tube techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use; alternatively a Solvent Purification System (Innovative Technologies) was also used.

Literature methods were used to prepare $[AuCl(tht)]$,³³ and $[M(H_2O)_2(dppp)](OTf)_2$ ($M = Pd$ (**A**), Pt (**B**)).³⁴ The phosphane gold chlorido precursors $[(AuCl)_2(\mu_2-dppm)]$ $[(AuCl)_2(\mu_2-dppip)]$, $[(AuCl)_2(\mu_2-dppe)]$, $[(AuCl)_2(\mu_2-dppp)]$, $[(AuCl)_2(\mu_2-dppb)]$, $[(AuCl)_3(\mu_3-triphos)]$, $[(AuCl)_3(\mu_3-triphosph)]$ were prepared from the reaction of $[AuCl(tht)]$ with the appropriate phosphane. All other reagents were obtained from commercial suppliers and used as received. Infrared spectra were recorded on a FT-IR 520 Nicolet Spectrophotometer. ¹H NMR (δ (TMS) = 0.0 ppm) and ³¹P{¹H} NMR (δ (85% H₃PO₄) = 0.0 ppm) spectra were obtained at 400 or 500 MHz with Varian and Bruker spectrometers at 25 °C unless otherwise stated. Elemental analyses of C, H, and N were carried out at the Centres Científics i Tecnològics (Universitat

de Barcelona). ESI-MS mass spectra of the metallaligands were recorded on a LC/MSD TOF Argilent Technologies 61969A spectrometer in H₂O:CH₃CN (1:1) solutions. In the case of the metallamacrocycles acetone solutions were used. Absorption spectra were recorded on a Shimadzu UV-2501PC and on a Cary 100 scan 388 Varian UV spectrophotometers and emission spectra on a Horiba-Jobin-Yvon SPEX Fluorolog 3.22 spectrofluorimeter. Quantum yields have been recorded on a Hamamatsu Absolute PL Quantum Yield Spectrometer C11347. Luminiscence lifetimes were measured on a JYF-DELTAPRO-NL equipment upon excitation the samples with a 280 nm Nanoled and collecting the decays through a bandpass filter of 400 nm.

X-Ray Structure Determination

Data for **1**, **2**, **3** and **5** were collected at 123.0 K on a dual source Rigaku Oxford SuperNova diffractometer equipped with an Atlas detector using mirror-monochromated Cu-*K*α radiation ($\lambda = 1.54184 \text{ \AA}$). All the data collection and reduction were done using the program CrysAlisPro³⁵ and the intensities were corrected for absorption using the analytical numeric face-index absorption correction method.³⁶ The structures were solved with intrinsic phasing method (SHELXT)³⁷ and refined by full-matrix least squares on F² using the OLEX2,³⁸ which utilizes the SHELXL module.³⁹ In all the structures, anisotropic displacement parameters were assigned to the non-hydrogen atoms. The hydrogen atoms were introduced at the ideal positions using riding models with U_{eq}(H) of 1.5U_{eq}(parent) for the terminal methyl groups and of 1.2U_{eq}(parent) for others. Restraint (ISOR and/or SIMU) commands were used where appropriate to suppress the alerts for large displacement parameter in checkcif for **1** and **5**.

Synthesis and Characterization

Synthesis of [(Au4-py)₂(CH)₂(μ₂-Au(PPh₂)₂)] (**1**)

Cs₂CO₃ (223 mg, 0.684 mmol) and 4-pyridylboronic acid (84 mg, 0.684 mmol) were suspended in isopropyl alcohol (20 mL) and [(AuCl)₂(μ₂-dppm)] (145 mg, 0.171 mmol) was added to the suspension. After 24 h of stirring at 80°C in the dark, the solvent was evaporated *in vacuo* and the residue was extracted 3 times (3 x 20 mL of CH₂Cl₂). The obtained solution was concentrated to dryness and washed with 10 ml of toluene. The remaining solid was dissolved in 5 mL of CH₂Cl₂ and the product was precipitated by addition of 50 mL of diethyl ether. A very pale pink solid was obtained that was filtered and dried *in vacuo*. Yield: 14% (20 mg). Anal. Found: C, 46.11; H, 2.97; N, 1.81; Calc. for C₆₀H₅₀Au₄N₂P₄: C, 46.05; H, 2.95;

N, 1.64%. IR $\nu_{\max}/\text{cm}^{-1}$ 1566 (py), 1480, 1434, 1099 (dppm). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K) 8.22 (d, 4H, $J = 4.8$ Hz, H_α py), 8.14-7.48 (m, 20H, Ph), 7.17 (m, 8H, Ph), 7.11 (d, 4H, $J = 4.8$ Hz, H_β py), 6.91-6.50 (m, 12H, Ph), 3.17 (q, 2H, $J(\text{P-H}) = 3.5$ Hz, CH). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.9 MHz, CDCl_3 , 298 K) 34.6 (s, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.7 MHz, CDCl_3 , 298 K) 147.5 (s, C_α py), 136.9 (s, C_β py), 136.0, 134.6 (m, C_q , py+Ph), 132.8, 130.6, 130.5, 128.8, 128.6 (s, CH, Ph), 25.0 (t, $J(\text{C-P}) = 9.7$ Hz, CH, dppm). MS ESI(+) m/z 1711.1634 (100%, $[\text{M}+\text{H}^+]^+$, calc. 1711.1659), 856.0853 (30%, $[\text{M}+2\text{H}^+]^{2+}$, calc. 856.0866).

Synthesis of $[(\text{Au4-py})_2(\mu_2\text{-dppip})]$ (1)

Cs_2CO_3 (223 mg, 0.684 mmol) and 4-pyridylboronic acid (84 mg, 0.684 mmol) were suspended in isopropyl alcohol (20 mL) and $[(\text{AuCl})_2(\mu_2\text{-dppip})]$ (150 mg, 0.171 mmol) was added to the suspension. After 24 h of stirring at 55°C in the dark, the solvent was evaporated *in vacuo* and the residue was extracted 3 times (3 x 20 mL of CH_2Cl_2). The obtained solution was concentrated to ca. 5 mL *in vacuo* and the product was precipitated by addition of 50 mL of hexane. The obtained white solid was filtered and dried *in vacuo*. Yield: 40% (66 mg). Anal. Found: C, 46.21; H, 3.52; N, 2.81; Calc. for $\text{C}_{37}\text{H}_{34}\text{Au}_2\text{N}_2\text{P}_2$: C, 46.17; H, 3.56; N, 2.91%. IR $\nu_{\max}/\text{cm}^{-1}$ 1509, 1433, 1091 (dppip). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K) 8.31 (d, 4H, $J = 4.0$ Hz, H_α py), 7.99-7.35 (m, 20H, Ph), 7.32 (m, 4H, H_β py), 1.72 (t, 6H, $J(\text{P-H}) = 14.1$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.9 MHz, CDCl_3 , 298 K) 54.4 (s, PPh_2). MS ESI(+) m/z 963.1645 (40%, $[\text{M}+\text{H}^+]^+$, calc. 963.1607), 482.0857 (100%, $[\text{M}+2\text{H}^+]^{2+}$, calc. 482.0842).

Synthesis of $[(\text{Au4-py})_2(\mu_2\text{-dppe})]$ (2)

Details of the synthesis of compound **1** were also applied to the preparation of this compound: From Cs_2CO_3 (340 mg, 1.04 mmol), 4-pyridylboronic acid (128 mg, 1.04 mmol) and $[(\text{AuCl})_2(\mu_2\text{-dppe})]$ (150 mg, 0.174 mmol). Yield: 50% (83 mg). Anal. Found: C, 45.71; H, 3.42; N, 2.93; Calc. for $\text{C}_{36}\text{H}_{32}\text{Au}_2\text{N}_2\text{P}_2$: C, 45.58; H, 3.38; N, 2.97%. IR $\nu_{\max}/\text{cm}^{-1}$ 1557 (py) 1479, 1434, 1102 (dppe). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 298 K) 8.40 (d, 4H, $J = 5.0$ Hz, H_α py), 7.73-7.44 (m, 20H, Ph), 7.39 (d, 4H, $J = 5.0$ Hz, H_β py), 2.77 (d, 4H, $J = 4.8$ Hz, CH_2). $^{31}\text{P}\{^1\text{H}\}$ -NMR (202.4 MHz, CDCl_3 , 298 K) 39.4 (s, PPh_2). MS ESI(+) m/z 949.1450 (25%, $[\text{M}+\text{H}^+]^+$, calc. 949.1450), 475.0748 (100%, $[\text{M}+2\text{H}^+]^{2+}$, calc. 475.0764).

Synthesis of $[(\text{Au4-py})_2(\mu_2\text{-dppp})]$ (3)

Details of the synthesis of compound **1** were also applied to the preparation of this compound: From Cs_2CO_3 (223 mg, 0.684 mmol), 4-pyridylboronic acid (84 mg, 0.684 mmol) and $[(\text{AuCl})_2(\mu_2\text{-dppp})]$ (150 mg, 0.171 mmol). Yield: 70% (115 mg). Anal. Found: C, 46.13; H, 3.53; N, 2.84; Calc. for $\text{C}_{37}\text{H}_{34}\text{Au}_2\text{N}_2\text{P}_2$: C, 46.17; H, 3.56; N, 2.91%. IR $\nu_{\max}/\text{cm}^{-1}$ 1565 (py)

1477, 1433, 1102 (dppp). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K) 8.30 (d, 4H, $J = 4.7$ Hz, H_α py), 7.73-7.34 (m, 24H, Ph + H_β py), 3.07 (q, 4H, $J = 7.2$ Hz, $\text{CH}_2\text{-PPh}_2$), (m, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (161.9 MHz, CDCl_3 , 298 K) 32.6 (s, PPh_2). MS ESI(+) m/z 963.1582 (10%, $[\text{M}+\text{H}^+]^+$, calc. 963.1607), 482.0833 (100%, $[\text{M}+2\text{H}^+]^{2+}$, calc. 482.0842).

Synthesis of $[(\text{Au4-py})_2(\mu_2\text{-dppb})]$ (4)

Details of the synthesis of compound **1** were also applied to the preparation of this compound: From Cs_2CO_3 (495 mg, 1.52 mmol), 4-pyridylboronic acid (187 mg, 1.52 mmol) and $[(\text{AuCl})_2(\mu_2\text{-dppb})]$ (150 mg, 0.152 mmol). Yield: 55% (82 mg). Anal. Found: C, 46.33; H, 3.76; N, 2.83; Calc. for $\text{C}_{38}\text{H}_{36}\text{Au}_2\text{N}_2\text{P}_2$: C, 46.73; H, 3.72; N, 2.87%. IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1568 (py) 1481, 1435, 1103 (dppb). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K) 8.38 (d, 4H, $J = 3.4$ Hz, H_α py), 7.69-7.42 (m, 20H, Ph), 7.38, (t, 4H, $J = 5.0$ Hz, H_β py), 2.47 (q, 4H, $J = 8.7$ Hz, $\text{CH}_2\text{-PPh}_2$), 1.89 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$), $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (161.9 MHz, CDCl_3 , 298 K) 37.8 (s, PPh_2). MS ESI(+) m/z 977.1745 (80%, $[\text{M}+\text{H}^+]^+$, calc. 977.1763), 489.0915 (100%, $[\text{M}+2\text{H}^+]^{2+}$, calc. 489.0920).

Synthesis of $[(\text{Au4-py})_3(\mu_3\text{-triphos})]$ (5)

Cs_2CO_3 (220 mg, 0.675 mmol) and 4-pyridylboronic acid (83 mg, 0.675 mmol) were suspended in isopropyl alcohol (20 mL) and $[(\text{AuCl})_3(\mu_3\text{-triphos})]$ (150 mg, 0.113 mmol) was added to the suspension. After 72 h of stirring at 55°C in the dark, the solvent was evaporated *in vacuo* and the residue was extracted 3 times (3 x 20 mL of CH_2Cl_2). The obtained solution was concentrated to ca. 5 mL *in vacuo* and the product was precipitated by addition of 50 mL of hexane. The obtained white solid was filtered and dried *in vacuo*. Yield: 60% (98 mg). Anal. Found: C, 46.29; H, 3.51; N, 2.94; Calc. for $\text{C}_{56}\text{H}_{51}\text{Au}_3\text{N}_3\text{P}_3$: C, 46.39; H, 3.55; N, 2.90%. IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1576 (py), 1434, 1099 (triphos). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K) 8.22 (m, 6H, H_α py), 7.66-7.27 (m, 30H, Ph), 7.15 (t, 6H, $J = 5.5$ Hz, H_β py), 3.27 (d, 6H, $^2J(\text{P-H}) = 10.2$ Hz, CH_2), 1.04 (s, 3H, CH_3). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (161.9 MHz, CDCl_3 , 298 K) 25.3 (s, PPh_2). MS ESI(+) m/z 1450.2357 (25%, $[\text{M}+\text{H}^+]^+$, calc. 1450.2365), 725.6226 (100%, $[\text{M}+2\text{H}^+]^{2+}$, calc. 725.6219), 484.0839 (30%, $[\text{M}+3\text{H}^+]^{3+}$, calc. 484.0842).

Synthesis of $[(\text{Au4-py})_3(\mu_3\text{-triphosph})]$ (6)

Details of the synthesis of compound **5** were also applied to the preparation of this compound: From Cs_2CO_3 (220 mg, 0.675 mmol), 4-pyridylboronic acid (83 mg, 0.675 mmol) and $[(\text{AuCl})_3(\mu_3\text{-triphosph})]$ (150 mg, 0.113 mmol). Yield: 35% (58 mg). Anal. Found: C, 46.89; H, 3.20; N, 2.92; Calc. for $\text{C}_{57}\text{H}_{45}\text{Au}_3\text{N}_3\text{P}_3$: C, 47.03; H, 3.12; N, 2.89%. IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1565 (py), 1480, 1436, 1100 (triphosph). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K) 8.39 (d, 6H, $J = 4.7$

Hz, H_{α} py), 7.75 (t, 3H, $J = 11.0$ Hz, $C_6H_3P_3$), 7.50-7.37 (m, 30H, Ph), 7.22 (t, 6H, $J = 4.7$ Hz, H_{β} py). $^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$, 298 K) 43.5 (s, PPh_2). MS ESI(+) m/z 1456.1896 (40%, $[M+H]^+$, calc. 1456.1896), 728.5976 (100%, $[M+2H]^{2+}$, calc. 728.5984), 486.0670 (15%, $[M+3H]^{3+}$, calc. 486.0686) .

Synthesis of $\{[(Au4-py)_2(\mu_2-dppip)]_2\{Pd(dppp)\}_2\}(CF_3SO_3)_4$ (1_2A_2): $[(Au4-py)_2(\mu_2-dppip)]$ (**1**) (10 mg, 0.01 mmol) and $[Pd(dppp)(H_2O)_2](CF_3SO_3)_2$ (**A**) (9 mg, 0.01 mmol) were dissolved in 10 mL of dichloromethane at room temperature. After 1 h of stirring the reaction mixture was concentrated to 3 mL *in vacuo* and an off-white solid was precipitated by addition of 20 mL of diethyl ether. The obtained product was filtered and dried *in vacuo*. Yield: 80% (14 mg). IR ν_{max}/cm^{-1} 1587 (py), 1482, 1437, 1100 (dppip), 1261, 1156 ($CF_3SO_3^-$). 1H -NMR (400 MHz, $CDCl_3$, 298 K) 8.46 (s br, 8H, H_{α} py), 7.85-7.31 (m, 80, PPh_2), 6.98 (s br, 8H, H_{β} py), 3.14 (m, 8H, P- $CH_2-CH_2-CH_2-P$, dppp), 2.25 (m br, 4H, P- $CH_2-CH_2-CH_2-P$, dppp). $^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$, 298 K) 55.9 (s, dppip), 6.5 (s, dppp). MS ESI(+) m/z 3409.260 ($[M-CF_3SO_3]^-$, calc. 3409.276), 1630.149 ($[M-2CF_3SO_3]^{2+}$, calc. 1630.162), 1037.112 ($[M-3CF_3SO_3]^{3+}$, calc. 1037.124) .

Compounds 1_2B_2 , 2_2A_2 , 2_2B_2 , 3_2A_2 and 3_2B_2 were synthesized following the same procedure described for compound 1_2A_2

Synthesis of $\{[(Au4-py)_2(\mu_2-dppip)]_2\{Pt(dppp)\}_2\}(CF_3SO_3)_4$ (1_2B_2): From $[(Au4-py)_2(\mu_2-dppip)]$ (**1**) (10 mg, 0.01 mmol) and $[Pt(dppp)(H_2O)_2](CF_3SO_3)_2$ (**A**) (10 mg, 0.01 mmol) 1_2B_2 was obtained as a white solid. Yield: 82% (16 mg). IR ν_{max}/cm^{-1} 1590 (py), 1482, 1437, 1101 (dppip), 1261, 1156 ($CF_3SO_3^-$). 1H -NMR (400 MHz, $CDCl_3$, 298 K) 8.48 (s br, 8H, H_{α} py), 7.72-7.30 (m, 80, PPh_2), 7.05 (s br, 8H, H_{β} py), 3.22 (m, 8H, P- $CH_2-CH_2-CH_2-P$, dppp), 2.24 (m br, 4H, P- $CH_2-CH_2-CH_2-P$, dppp). $^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$, 298 K) 55.8 (s, dppip), 14.4 (s, $J(^{31}P-^{195}Pt) = 2964$ Hz, dppp). MS ESI(+) m/z 1718.718 ($[M-2CF_3SO_3]^{2+}$, calc 1718.721); 1096.163 ($[M-3CF_3SO_3]^{3+}$, calc 1096.163); 785.132 ($[M-4CF_3SO_3]^{4+}$, calc 784.884); 482.0829 ($[1+2H]^{2+}$, calc. 482.0842).

Synthesis of $\{[(Au4-py)_2(\mu_2-dppe)]_2\{Pd(dppp)\}_2\}(CF_3SO_3)_4$ (2_2A_2): From $[(Au4-py)_2(\mu_2-dppe)]$ (**2**) (10 mg, 0.01 mmol) and $[Pd(dppp)(H_2O)_2](CF_3SO_3)_2$ (**A**) (9 mg, 0.01 mmol) 2_2A_2 was obtained as a white solid. Yield: 56% (10 mg). IR ν_{max}/cm^{-1} 1598 (py), 1483, 1436, 1102 (dppe), 1260, 1156 ($CF_3SO_3^-$). 1H -NMR (500 MHz, $CDCl_3$, 298 K) 8.38 (d, 8H, $J(H-H) = 4.4$ Hz, H_{α} py), 7.73-7.34 + 7.18-7.15 (m, 80, PPh_2), 6.76 (d, 8H, $J(H-H) = 4.8$ Hz, H_{β} py), 3.15 (s br, 8H, P- $CH_2-CH_2-CH_2-P$, dppp), 2.68 (d, 8H, $J(H-H) = 11.8$ Hz, P- CH_2-CH_2-P , dppe), 2.30 (m br, 4H, P- $CH_2-CH_2-CH_2-P$, dppp). $^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$, 298 K) 35.4 (s,

dppe), 6.0 (s, dppp). MS ESI(+) m/z 1616.146 ($[M-2CF_3SO_3]^{2+}$, calc 1616.146); 949.143 ($[2+H^+]^+$, calc. 949.145), 475.076 ($[2+2H^+]^{2+}$, calc. 475.076).

Synthesis of $\{[(Au4-py)_2(\mu_2-dppe)]_2\{Pt(dppp)\}_2\}(CF_3SO_3)_4$ ($2B_2$). From $[(Au4-py)_2(\mu_2-dppe)]$ (**2**) (10 mg, 0.01 mmol) and $[Pt(dppp)(H_2O)_2](CF_3SO_3)_2$ (**B**) (10 mg, 0.01 mmol) $2B_2$ was obtained as a white solid. Yield: 61% (12 mg). IR ν_{max}/cm^{-1} 1589 (py), 1483, 1437, 1103 (dppe), 1259, 1156 ($CF_3SO_3^-$). 1H -NMR (500 MHz, $CDCl_3$, 298 K) 8.38 (d, 8H, $J(H-H) = 5.5$ Hz, H_α py), 7.75-7.32 + 7.22-7.18 (m, 80, PPh_2), 6.81 (t, 8H, $J(H-H) = 4.9$ Hz H_β py), 3.23 (s br, 8H, P- $CH_2-CH_2-CH_2$ -P, dppp), 2.71 (d, 8H, $J(H-H) = 13.9$ Hz P- CH_2-CH_2 -P, dppe), 2.27 (m br, 4H, P- $CH_2-CH_2-CH_2$ -P, dppp). $^{31}P\{^1H\}$ -NMR (202.4 MHz, $CDCl_3$, 298 K) 35.2 (s, dppe), -14.6 (s, $^1J(^{31}P-^{195}Pt) = 3020$ Hz, dppp(Pt)). MS ESI(+) m/z 1705.206 ($[M-2CF_3SO_3]^{2+}$, calc 1616.146); 1086.821 ($[M-3CF_3SO_3]^{3+}$, calc 1086.820); 949.143 ($[2+H^+]^+$, calc. 949.145), 475.076 ($[2+2H^+]^{2+}$, calc. 475.076).

Synthesis of $\{[(Au4-py)_2(\mu_2-dppp)]_2\{Pd(dppp)\}_2\}(CF_3SO_3)_4$ ($3A_2$). From $[(Au4-py)_2(\mu_2-dppp)]$ (**2**) (10 mg, 0.01 mmol) and $[Pd(dppp)(H_2O)_2](CF_3SO_3)_2$ (**A**) (9 mg, 0.01 mmol) $3A_2$ was obtained as a white solid. Yield: 80% (15 mg). IR ν_{max}/cm^{-1} 1586 (py), 1483, 1437, 1103 (dppp), 1260, 1156 ($CF_3SO_3^-$). 1H -NMR (400 MHz, $CDCl_3$, 298 K) 8.33 (s br, 8H, H_α py), 7.63-7.23 (m, PPh_2 superimposed with the residual protons of $CDCl_3$), 6.80 (m, 8H, H_β py), 3.13 (s br, 8H, AuP- $CH_2-CH_2-CH_2$ -PAu, dppp), 2.87 (m, 8H, PdP- $CH_2-CH_2-CH_2$ -P, dppp), 2.19 (m br, 4H, AuP- $CH_2-CH_2-CH_2$ -PAu, dppp), 1.76 (m br, 4H, PdP- $CH_2-CH_2-CH_2$ -P, dppp). $^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$, 298 K) 30.7 (s, dppp(Au)), 6.1 (s, dppp(Pd)). MS ESI(+) m/z 1037.1224 ($[M-3CF_3SO_3]^{3+}$, calc 1037.124); 963.1590 ($[3+H^+]^+$, calc. 963.1607), 482.0845 ($[3+2H^+]^{2+}$, calc. 482.0842).

Synthesis of $\{[(Au4-py)_2(\mu_2-dppp)]_2\{Pt(dppp)\}_2\}(CF_3SO_3)_4$ ($3B_2$). From $[(Au4-py)_2(\mu_2-dppp)]$ (**2**) (10 mg, 0.01 mmol) and $[Pt(dppp)(H_2O)_2](CF_3SO_3)_2$ (**B**) (10 mg, 0.01 mmol) $3B_2$ was obtained as a white solid. Yield: 81% (16 mg). IR ν_{max}/cm^{-1} 1590 (py), 1483, 1437, 1103 (dppp), 1260, 1156 ($CF_3SO_3^-$). 1H -NMR (400 MHz, $CDCl_3$, 298 K) 8.30 (d, 8H, $J = 5.4$ Hz, H_α py), 7.67-7.24 (m, PPh_2 superimposed with the residual protons of $CDCl_3$), 6.82 (t, 8H, $J = 5.3$ Hz, H_β py), 3.20 (s br, 8H, P- $CH_2-CH_2-CH_2$ -P, dppp(Au)), 2.89 (q, 8H, $J = 7.5$ Hz, P- $CH_2-CH_2-CH_2$ -P, dppp(Pt)), 2.17 (m br, 4H, P- $CH_2-CH_2-CH_2$ -P, dppp(Au)), 1.78 (m, 4H, P- $CH_2-CH_2-CH_2$ -P, dppp(Pt)). $^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$, 298 K) 30.3 (s, dppp(Au)), -14.3 (s, $^1J(^{31}P-^{195}Pt) = 3019$ Hz, dppp(Pt)). MS ESI(+) m/z 1719.221 ($[M-2CF_3SO_3]^{2+}$, calc 1718.723); 1096.164 ($[M-3CF_3SO_3]^{3+}$, calc 1096.164); 963.159 ($[3+H^+]^+$, calc. 963.161);

784.881 ($[\text{M}-4\text{CF}_3\text{SO}_3]^{4+}$ superimposed with $[\mathbf{3}+\mathbf{B}-2\text{CF}_3\text{SO}_3]^{2+}$, calc 784.885); 482.083 ($[\mathbf{3}+2\text{H}^+]^{2+}$, calc. 482.084).

Synthesis of $[(\text{Au4-py})_3(\mu_3\text{-triphosph})]_2[\text{Pd}(\text{dppp})]_3(\text{CF}_3\text{SO}_3)_6$ ($\mathbf{6}_2\mathbf{A}_3$). $[(\text{Au4-py})_3(\mu_2\text{-triphosph})]$ ($\mathbf{6}$) (15 mg, 0.010 mmol) and $[\text{Pd}(\text{dppp})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ (\mathbf{A}) (13 mg, 0.015 mmol) were suspended in 5 mL of isopropyl alcohol and the resulting mixture was irradiated by microwave (150W, 25 °C) for 15 min. After evaporation *in vacuo* and the residue was extracted three times with dichloromethane (3x10 mL). The combined extracts were concentrated to 5 mL and an off-white solid was precipitated by addition of 20 mL of diethyl ether. The obtained product was filtered and dried *in vacuo*. Yield: 82% (17 mg). IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1586 (py), 1480, 1436, 1101 (triphosph), 1254, 1154 (CF_3SO_3^-). $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2 , 298 K) 8.47 (d, 12H, $J = 5.3$ Hz, H_α py), 7.70-7.15 (m, 126H, $\text{PPh}_2 + \text{C}_6\text{H}_3\text{P}_3$), 6.90 (t, 12H, $J = 5.4$ Hz, H_β py), 3.15 (s br, 12H, $\text{P-CH}_2\text{-CH}_2\text{-CH}_2\text{-P}$, dppp), 2.23 (m br, 6H, $\text{P-CH}_2\text{-CH}_2\text{-CH}_2\text{-P}$, dppp). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (161.9 MHz, CD_2Cl_2 , 298 K) 42.8 (s, triphosph), 6.2 (s, dppp). MS ESI(+) m/z 2531.64 ($[\text{M}-2\text{CF}_3\text{SO}_3]^{2+}$, calc 2532.17); 1638.44 ($[\text{M}-3\text{CF}_3\text{SO}_3]^{3+}$, calc 1638.46); 1191.34 ($[\text{M}-4\text{CF}_3\text{SO}_3]^{4+}$, calc 1191.61)

Synthesis of $[(\text{Au4-py})_3(\mu_3\text{-triphosph})]_2[\text{Pt}(\text{dppp})]_3(\text{CF}_3\text{SO}_3)_6$ ($\mathbf{6}_2\mathbf{B}_3$). $[(\text{Au4-py})_3(\mu_2\text{-triphosph})]$ ($\mathbf{6}$) (15 mg, 0.010 mmol) and $[\text{Pt}(\text{dppp})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ (\mathbf{B}) (14 mg, 0.015) were dissolved in 10 mL of dichloromethane at room temperature. After 1 h of stirring the reaction mixture was concentrated to 3 mL *in vacuo* and an off-white solid was precipitated by addition of 20 mL of diethyl ether. The obtained product was filtered and dried *in vacuo*. Yield: 72% (20 mg). IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1589 (py), 1482, 1437, 1102 (triphosph), 1258, 1157 (CF_3SO_3^-). $^1\text{H-NMR}$ (250 MHz, CD_2Cl_2 , 298 K) 8.47 (s br, 12H, H_α py), 7.87-7.21 (m, 126H, $\text{PPh}_2 + \text{C}_6\text{H}_3\text{P}_3$), 6.90 (t, 12H, $J = 5.3$ Hz, H_β py), 3.23 (s br, 12H, $\text{P-CH}_2\text{-CH}_2\text{-CH}_2\text{-P}$, dppp), 2.21 (m br, 6H, $\text{P-CH}_2\text{-CH}_2\text{-CH}_2\text{-P}$, dppp). $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (101.2 MHz, CD_2Cl_2 , 298 K) 43.3 (s, triphosph), 14.0 (s, $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3055$ Hz, dppp). MS ESI(+) m/z 2664.764 ($[\text{M}-2\text{CF}_3\text{SO}_3]^{2+}$, calc 2663.762); 1726.854 ($[\text{M}-3\text{CF}_3\text{SO}_3]^{3+}$, calc 1726.857); 1257.903 ($[\text{M}-4\text{CF}_3\text{SO}_3]^{4+}$, calc 1257.905).

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References

- (1) (a) C. R. P. Fulong, S. Kim, A. E. Friedman and T. R. Cook, *Front. Chem.*, 2019, **7**;
(b) J. Gil-Rubio and J. Vicente, *Chem.-Eur. J.*, 2018, **24**, 32-46; (c) R. J. Puddephatt, *J. Organomet. Chem.*, 2015, **792**, 13-24; (d) V. Camara, N. Barquero, D. Bautista, J. Gil-Rubio and J. Vicente, *Chem.-Eur. J.*, 2015, **21**, 1992-2002; (e) R. J. Puddephatt, *Chem. Soc. Rev.*, 2008, **37**, 2012-2027.
- (2) (a) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931-1951; (b) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370-412.
- (3) (a) B. Li, T. He, Y. Fan, X. Yuan, H. Qiu and S. Yin, *Chem. Commun.*, 2019, **55**, 8036-8059; (b) S. Pullen and G. H. Clever, *Acc. Chem. Res.*, 2018, **51**, 3052-3064; (c) S.-L. Huang, T. S. A. Hor and G.-X. Jin, *Coord. Chem. Rev.*, 2017, **333**, 1-26; (d) T. R. Cook and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001-7045.
- (4) (a) M. J. Calhorda, C. Ceamanos, O. Crespo, M. C. Gimeno, A. Laguna, C. Larraz, P. D. Vaz and M. D. Villacampa, *Inorg. Chem.*, 2010, **49**, 8255-8269; (b) S. S. Nurttilla, W. Brenner, J. Mosquera, K. M. van Vliet, J. R. Nitschke and J. N. H. Reek, *Chem. - Eur. J.*, 2019, **25**, 609-620; (c) I. D. Strel'nik, V. V. Gurzhiy, V. V. Sizov, E. I. Musina, A. A. Karasik, S. P. Tunik and E. V. Grachova, *CrystEngComm*, 2016, **18**, 7629-7635; (d) A. Luengo, V. Fernández-Moreira, I. Marzo and M. C. Gimeno, *Inorg. Chem.*, 2017, **56**, 15159-15170; (e) K. Chen and V. J. Catalano, *Eur. J. Inorg. Chem.*, 2015, **2015**, 5254-5261; (f) J. A. Casares, P. Espinet, J. M. Martín-Álvarez and V. Santos, *Inorg. Chem.*, 2006, **45**, 6628-6636.
- (5) (a) S. Onaka, M. Yaguchi, R. Yamauchi, T. Ozeki, M. Ito, T. Sunahara, Y. Sugiura, M. Shiotsuka, M. Horibe, K. Okazaki, A. Iida, H. Chiba, K. Inoue, H. Imai and K. Sako, *J. Organomet. Chem.*, 2005, **690**, 57-68; (b) K. Nunokawa, S. Onaka, Y. Mizuno, K. Okazaki, T. Sunahara, M. Ito, M. Yaguchi, H. Imai, K. Inoue, T. Ozeki, H. Chiba and T. Yosida, *J. Organomet. Chem.*, 2005, **690**, 48-56; (c) R. E. Cordero-Rivera, D. Rendón-Nava, C. Ángel-Jijón, O. R. Suárez-Castillo and D. Mendoza-Espinosa, *Organometallics*, 2020, **39**, 1887-1895.
- (6) (a) V. J. Catalano and A. O. Etogo, *Inorg. Chem.*, 2007, **46**, 5608-5615; (b) V. J. Catalano and A. O. Etogo, *J. Organomet. Chem.*, 2005, **690**, 6041-6050; (c) V. J.

- Catalano, M. A. Malwitz and A. O. Etogo, *Inorg. Chem.*, 2004, **43**, 5714-5724; (d) C. E. Strasser and V. J. Catalano, *Inorg. Chem.*, 2011, **50**, 11228-11234.
- (7) (a) M. C. Blanco, J. Camara, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. Lopez-de-Luzuriaga, M. E. Olmos and M. D. Villacampa, *Organometallics*, 2012, **31**, 2597-2605; (b) M. Ferrer, A. Gutierrez, L. Rodriguez, O. Rossell, J. C. Lima, M. Font-Bardia and X. Solans, *Eur. J. Inorg. Chem.*, 2008, 2899-2909; (c) M. Ferrer, L. Rodriguez, O. Rossell, F. Pina, J. C. Lima, M. F. Bardia and X. Solans, *J. Organomet. Chem.*, 2003, **678**, 82-89.
- (8) M. Ferrer, A. Gutierrez, M. Mounir, L. Rodriguez, O. Rossell, M. Font-Bardia, P. Gomez-Sal, A. Martin and X. Solans, *Organometallics*, 2011, **30**, 3419-3429.
- (9) D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Inorg. Chem.*, 2012, **51**, 8394-8401.
- (10) H. K. Lenker, T. G. Gray and R. A. Stockland, *Dalton Trans.*, 2012, **41**, 13274-13276.
- (11) E. J. Fernandez, A. Laguna and M. E. Olmos, *Adv. Organomet. Chem.*, 2005, **52**, 77-141.
- (12) (a) D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem. Int. Ed.*, 2006, **45**, 8188-8191; (b) D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2009, **28**, 1666-1674; (c) J. E. Heckler, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem. Int. Ed.*, 2012, **51**, 5924-5928.
- (13) M. Ferrer, A. Gutierrez, L. Rodriguez, O. Rossell, E. Ruiz, M. Engeser, Y. Lorenz, R. Schilling, P. Gomez-Sal and A. Martin, *Organometallics*, 2012, **31**, 1533-1545.
- (14) L. Rodriguez, J. C. Lima, M. Ferrer, O. Rossell and M. Engeser, *Inorg. Chim. Acta*, 2012, **381**, 195-202.
- (15) L. Rodríguez, M. Ferrer, R. Crehuet, J. Anglada and J. C. Lima, *Inorg. Chem.*, 2012, **51**, 7636-7641.
- (16) (a) T. G. Gray, *Comments Inorg. Chem.*, 2007, **28**, 181-212; (b) A. S. K. Hashmi, T. D. Ramamurthi and F. Rominger, *J. Organomet. Chem.*, 2009, **694**, 592-597; (c) D. V. Partyka, T. S. Teets, M. Zeller, J. B. Updegraff, A. D. Hunter and T. G. Gray, *Chem.-Eur. J.*, 2012, **18**, 2100-2112.
- (17) R. Usón, A. Laguna, M. Laguna and M. C. Gimeno, *J. Chem. Soc., Dalton Trans.*, 1989, 1883-1886.
- (18) E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, J. M. López-de-Luzuriaga and M. A. Rodríguez, *Chem. Ber.*, 1995, **128**, 121-124.

- (19) R. Usón, A. Laguna, M. Laguna, M. a. C. Gimeno, P. G. Jones, C. Fittschen and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1986, 509-510.
- (20) B.-C. Tzeng, B.-S. Chen, C.-K. Chen, Y.-P. Chang, W.-C. Tzeng, T.-Y. Lin, G.-H. Lee, P.-T. Chou, Y.-J. Fu and A. H.-H. Chang, *Inorg. Chem.*, 2011, **50**, 5379-5388.
- (21) A. Pintado-Alba, H. de la Riva, M. Nieuwhuyzen, D. Bautista, P. R. Raithby, H. A. Sparkes, S. J. Teat, J. M. Lopez-de-Luzuriaga and M. C. Lagunas, *Dalton Trans.*, 2004, 3459-3467.
- (22) M. Bardaji, P. G. Jones, A. Laguna, A. Moracho and A. K. Fischer, *J. Organomet. Chem.*, 2002, **648**, 1-7.
- (23) E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesivilla and C. Guastini, *Organometallics*, 1989, **8**, 1067-1079.
- (24) W. J. Wolf, M. S. Winston and F. D. Toste, *Nature Chemistry*, 2014, **6**, 159-164.
- (25) C. H. Li, S. C. F. Kui, I. H. T. Sham, S. S. Y. Chui and C. M. Che, *Eur. J. Inorg. Chem.*, 2008, 2421-2428.
- (26) (a) Q.-Y. Cao, B. Yin and J.-H. Liu, *Acta Cryst.*, 2006, **E62**, m2730-m2731; (b) A. Pons, O. Rossell, M. Seco, X. Solans and M. FontBardia, *J. Organomet. Chem.*, 1996, **514**, 177-182; (c) L. C. Porter, M. N. I. Khan, C. King and J. P. Fackler, Jr, *Acta Cryst.*, 1989, **C45**, 947-949.
- (27) (a) S. Ghosh, S. R. Batten, D. R. Turner and P. S. Mukherjee, *Organometallics*, 2007, **26**, 3252-3255; (b) D. Bardhan and D. K. Chand, *Chem. -Eur. J.*, 2019, **25**, 12241-12269; (c) T. H. Noh, E. Heo, K. H. Park and O. S. Jung, *J. Am. Chem. Soc.*, 2011, **133**, 1236-1239; (d) S. Chakraborty, S. Mondal, Q. J. Li and N. Das, *Tetrahedron Lett.*, 2013, **54**, 1681-1685.
- (28) Molecular modelling was carried out using Spartan'10 V1.1.0 for Mac as software. After a optimisation at MM+ molecular mechanics leve, DFT calculations were carried out with the Spartan software using B3LYP hybrid functional.
- (29) (a) S. Bhargava, K. Kitadai, T. Masashi, D. W. Drumm, S. P. Russo, V. W. W. Yam, T. K. M. Lee, J. Wagler and N. Mirzadeh, *Dalton Trans.*, 2012, **41**, 4789-4798; (b) R. V. Bojan, R. Czerwieniec, A. Laguna, T. Lasanta, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and H. Yersin, *Dalton Trans.*, 2013, **42**, 4267-4277.
- (30) (a) N. Kathewad, N. Kumar, R. Dasgupta, M. Ghosh, S. Pal and S. Khan, *Dalton Trans.*, 2019, **48**, 7274-7280; (b) M. C. Lagunas, C. M. Fierro, A. Pintado-Alba, H. de la Riva and S. Betanzos-Lara, *Gold Bull*, 2007, **40**, 135-141; (c) D. Li, C.-M. Che, H.-L. Kwong and V. W.-W. Yam, *J. Chem. Soc., Dalton Trans.*, 1992, 3325-3329.

- (31) M. J. Mayoral, P. Ovejero, R. Criado, M. C. Lagunas, A. Pintado-Alba, M. R. Torres and M. Cano, *J. Organomet. Chem.*, 2011, **696**, 2789-2796.
- (32) The emission spectra of the chlorido gold(I) precursors have been recorded in dichloromethane solution at 298 K exciting at the absorption maxima.
- (33) R. Usón and A. Laguna, *Organomet. Synth.*, 1986, **3**, 322-342.
- (34) P. J. Stang, D. H. Cao, S. Saito and A. M. Arif, *J. Am. Chem. Soc.*, 1995, **117**, 6273-6283.
- (35) *CrysAlisPro 2016*, Rigaku Oxford Diffraction, Version 1.171.38.43.
- (36) R. C. Clark and J. S. Reid, *Acta Cryst.*, 1995, **A51**, 887-897.
- (37) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
- (38) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
- (39) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.