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# Gold(I) complexes with multifunctional phosphane ligands: Synthesis and catalysis

Andrea Biffis<sup>a,\*</sup>, Marco Baron<sup>a</sup>, Cristina Tubaro<sup>a,b</sup>, Marzio Rancan<sup>b</sup>, Lidia Armelao<sup>a,b</sup>, Anatoliy Marchenko<sup>c</sup>, Georgyi Koidan<sup>c</sup>, Anastasiia N. Hurieva<sup>c</sup>, Aleksandr Kostyuk<sup>c</sup>

<sup>a</sup> Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy

<sup>b</sup> Institute of Condensed Matter Chemistry and Technologies for Energy (ICMATE), National Research Council (CNR), Via F. Marzolo 1, 35131 Padova, Italy

<sup>c</sup> Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska 5, Kyiv-94 02660, Ukraine

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Dedicated to Prof. Maurizio Peruzzini on the occasion of his  $65^{\rm th}$  birthday.

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ABSTRACT

Two novel gold(I) complexes with a phosphoguanidine ligand and with a novel cationic phosphane ligand have been prepared and structurally characterized. The phosphoguanidine ligand supports oxidative addition of biphenylene to the gold(I) centre, though the yield of the reaction is low. The phopshoguanidine gold(I) complexes is also able to efficiently catalyze the hydroamination of phenylacetylene with mesitylamine, whereas the gold(I) complex with the cationic phosphane ligand, due to its more electron-poor character, promotes the hydroarylation of ethyl propiolate with mesitylene.

1. Introduction

The last decades have witnessed the steady development of a great variety of heteroleptic polydentate ligands for transition metal complexes [1-3], and more recently a growing number of applications of these ligands to the preparation of coordination compounds of gold(III) [4,5] and most notably gold(I) [6-15]. Two Lewis-basic moieties with different characteristics on the same ligand can serve different purposes in the context of gold(I) coordination chemistry. For example, since the two coordination sites can bind to a gold(I) halide with different strength, they can behave as hemilabile ligands, in which one of the moieties is more strongly coordinated to the gold(I) centre whereas the other one interacts more weakly; consequently, complexes with a distorted trigonal planar coordination geometry can be prepared, which often exhibit peculiar physico-chemical properties, such as a strong luminescence [6]. Alternatively, a gold centre can bind only to one coordination site of the ligand, whereas the other Lewis-basic moiety remains pendant and can coordinate a second metal centre with different characteristics [7-9], or it can direct and activate the attack of an external reagent to a substrate precoordinated to the gold complex, for example by acting as a hydrogen bond acceptor [10–12]. Finally, gold(I) can bind only to one Lewis-basic moiety of the ligand and interact with the second one when it becomes oxidized to gold(III); at this point, the ligand can coordinate in a chelating bidentate fashion, thereupon stabilizing the complex. Following pioneering examples of Huang et al. [13,14], a notable example of this behaviour has been quite recently provided by Abdallah et al. with a gold(I) phosphane complex bearing a pendant tertiary arylamino moiety, in which oxidative addition at gold (II) is facilitated by chelate coordination of the amino moiety to the gold (III) complex product [15].

In the context of this growing interest for gold(I) complexes with heteroleptic polydentate ligands, we wish to report here on the preparation of gold(I) complexes with two novel multifunctional phosphane ligands and on their properties, reactivity and preliminary evaluation as catalysts for hydrofunctionalization reactions.

#### 2. Results and discussion

We have considered two ligands in this study, namely 1 and 2 (Scheme 1). Ligand 1 is a phosphoguanidine ligand whose chelate

\* Corresponding author. E-mail address: andrea.biffis@unipd.it (A. Biffis).

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Research paper





Scheme 1. Phosphane ligands employed in this study.

complex with palladium(II) has been already investigated by our group and found to be an active catalyst for alkyne hydroamination reactions [16]. It belongs to a class of open chain, P.N 1.3-ligands, which comprises also 2-phosphanoimidazoles, 2-phosphanopyridines and phosphoamidines: examples of coordination chemistry of gold(I) with these categories of ligands have been also published recently [17-20]. Ligand 2 is instead a novel example of cationic phosphane ligand deriving directly from [1,2,4]triazolo[4,3-a]pyridine [21], whose coordination chemistry has never been investigated before. It is an interesting potential ligand: being cationic, the ligand can be expected to feature a lower electron-donating capability, which may be useful for certain applications (see below); examples of the successful application of gold (I) complexes with cationic phosphane ligands to selected chemical reactions have been reported recently [22–24]. Furthermore, the presence of the positive charge can possibly endow the complex with water solubility. Finally, the C-H bond in 3-position of the heterocycle can be in principle deprotonated giving rise to a carbene moiety; attempts to deprotonate the free ligand actually have led up to now to decomposition [21], but deprotonation a gold(I) phosphane complex and/or in the presence of metal centres able to promptly coordinate to the carbene may result in stabilization of the carbene.

Simple ligand exchange using [AuCl(SMe<sub>2</sub>)] as gold precursor in dichloromethane at room temperature under light exclusion easily provides gold(I) complexes **3** and **4**, directly deriving from **1** and **2**, in good yield (Scheme 2). Recrystallization from acetonitrile/diethylether provided crystals suitable for structure determination.

Complex **3** (Fig. 1a), crystallizes in the monoclinic  $P2_1/n$  space group. The Au coordination geometry is linear (P1-Au1-Cl1 178.80(3)°) with Au1-P1 and Au1-Cl1 distances of 2.2473(5) Å and 2.2755(7) Å, respectively. Crystallization of complex **4** under slightly different conditions gave crystal structures **4a** and **4b** (Fig. 1b and 1c), respectively. The former, **4a**, crystallizes from a mixture of acetonitrile/diethylether as needle-like colourless crystals in the triclinic *P*-1 space group. The



latter, 4b, obtained as prism-like, colourless crystals, crystallizes in the monoclinic  $P2_1/n$  space group. The two structures present the same Au complex but 4b contains also an acetonitrile molecule associated to each complex unit. In both cases, a triflate anion is present in order to balance the positively charged nitrogen atom of ligand 2. In both structures, the Au coordination geometry is linear (P1-Au1-Cl1 of 173.82(5)° and 173.25(8)° for 4a and 4b, respectively) with Au1-P1 and Au1-Cl1 distances of 2.2301(14) Å and 2.2820(13) Å for 4a, and of 2.2286(19) Å and 2.275(2) Å in 4b. The two coordination complex moieties are very similar, as can be observed by their overlaid structures. The main difference is the relative orientation of the heterocycle unit, as can be seen in Fig. 1d. In fact, looking along the N1-P1 bond, in 4a the heterocycle is on the right of the Au1-Cl1 bond with a torsional angle of Cl1-Au1-P1-N1  $171.2(7)^{\circ}$ . In **4b**, the same angle is  $-147.1(6)^{\circ}$  and the heterocycle is on the left of the Au1-Cl1 bond. Table 1 summarizes the main distances and angles and Table 2 reports the main crystallographic and refinement information for compounds 3, 4a and 4b.

From the crystal structure of complex 3, it is apparent that no interaction is present between the gold(I) centre and the pendant imino group of the ligand. In order to investigate the possibility to produce chelate gold(III) complexes upon oxidation of gold and subsequent coordination of the imino moiety, complex 3 was subjected to reaction with several oxidants. We started by investigating reactions with Br<sub>2</sub> or PhICl<sub>2</sub>, which are commonly employed oxidants in the preparation of gold(III) compounds from gold(I) precursors [25,26]. Treatment of complex 3 with one equivalent of either of these reagents resulted however in decomposition of the complex. In the case of PhICl<sub>2</sub>, analysis of the <sup>31</sup>P NMR and of the ESI-MS spectra of the reaction mixture allowed to identify signals attributable to the free ligand and to a major product (<sup>31</sup>P NMR  $\delta$  142.72, *m/z* 371.10) interpretable in terms of an oxidized phosphorus species deriving from the ligand (PAd<sub>2</sub>Cl<sup>+</sup><sub>2</sub> in the ESI-MS spectrum). Thus, PhICl<sub>2</sub> seems to oxidize the phosphorus atom together with the gold(I) centre, and consequently triggers complex decomposition. Use of a milder oxidant such as Br2 provided no improvement, and complex product mixtures were obtained , from which it was not possible to identify any well-defined product.

We then resolved to change the procedure and to consider even weaker oxidants. Following the reaction protocol reported by Abdallah et al. [15], we reacted the complex at -80 °C with one equivalent of AgSbF<sub>6</sub> to remove the halide ligand, in the presence of organic molecules, such as 4-iodoanisole or biphenylene, amenable to undergo oxidative addition to gold(I) centres. In both cases extensive complex decomposition with formation of colloidal gold was observed when the reaction mixture was allowed to warm to room temperature, which is a confirmation of the expected low stability of the gold(I) cationic complex which forms upon chloride removal from 3. However, whereas with iodoanisole no sign of progress of an oxidative addition was observed in the reaction mixture, in the case of biphenylene definite evidence for the formation of an oxidative addition product was clearly obtained from the ESI-MS spectrum of the reaction mixture, in which a base peak at m/*z* 853.33 corresponding to complex **5** (Scheme 3) was clearly observed. Correspondingly, a new signal was also observed in the  $^{31}\mathrm{P}$  NMR spectrum of the reaction mixture at 70.6 ppm, which is compatible with a phosphane bound gold(III) cation [15]. Unfortunately, the yields of the compound were invariably low and the reaction was not clean, with several other lower molecular weight products being present in the reaction mixture, as apparent from the <sup>1</sup>H NMR. Consequently, it was not possible up to now to isolate and further characterize complex 5 or a derivative of it. We can conclude at the moment that ligand 1 is able to some extent to facilitate oxidative addition to gold(I) upon formation of a chelate complex, but that the rate of oxidative addition is much slower compared to the aminophosphine ligand employed by Abdallah et al., to the point that decomposition of the cationic gold(I) reagent derived from **3** becomes a serious competitive reaction. The reason for this different behaviour is presumably the strained 4-membered chelate complex that is formed with ligand 1.



Fig. 1. ORTEP drawing of a) complex 3; b) and c) complex 4 in its crystallographic forms 4a and 4b, respectively; d) overlay of structures 4a (dark cyan) and 4b (green). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The reactivity of complex **4** was instead briefly investigated relating to the possibility to deprotonate the CH bond in 3-position on the heterocyclic ring to produce a carbene moiety. Several bases were employed for the purpose, such as Na<sub>2</sub>CO<sub>3</sub>, NEt<sub>3</sub> and NaOAc, in the presence of metal complex precursors such as [AuCl(SMe<sub>2</sub>)], Pd(OAc)<sub>2</sub> or [Pd<sub>2</sub>(allyl)<sub>2</sub>Cl<sub>2</sub>] that should promptly coordinate the newly generated carbene and stabilize it. Unfortunately, all attempts invariably caused decomposition of complex **4** with formation of colloidal gold, with a decomposition rate depending on the employed base, and without any evidence of formation of the free carbene or of metal complexes thereof. Apparently, even starting from complex **4** it is not possible to form the carbene or to intercept it under any of the conditions employed.

Finally, we turned to the preliminary evaluation of complexes **3** and **4** as catalysts [27–29]. The catalytic performance of the two complexes in the hydroamination of alkynes [30] was considered first. Reaction of phenylacetylene with mesitylamine was employed as standard reaction (Scheme 4), for which there is considerable precedent in the literature with several benchmark gold catalysts with which to critically compare the recorded catalytic performance [31]. Complexes **3** and **4** were activated by reaction with one equivalent of AgSbF<sub>6</sub>, which removes the chloride ligand liberating the catalytically competent LAu<sup>+</sup> or LAu<sup>2+</sup> species, respectively. The reaction was carried out under neat conditions using 0.4 mol% catalyst, according to a protocol recently developed in our laboratories for dinuclear di-NHC gold(I) complexes as catalysts [32]. The results are reported in Table 3.

The recorded catalytic activity with complex 3 (TOF<sup>t=2h</sup> 17 h<sup>-1</sup>) compares favourably with most gold complexes with phosphane ligands reported in the literature [33], which under comparable reaction conditions (low temperature, absence of acid promoters) generally exhibit TOF values below 10 h<sup>-1</sup>. The recorded activity remains however markedly lower than the best gold-phosphane catalysts reported to date for this reaction, which are based on anionic or zwitterionic phosphanes and can reach TOFs up to  $10^2 \cdot 10^3$  h<sup>-1</sup> [34,35]. The reaction was also attempted with a secondary amine such as *N*-methylaniline. However,

reaction with this substrate reportedly requires a higher reaction temperature (80  $^{\circ}$ C) which was not sustained by catalyst **3**: catalyst decomposition with formation of colloidal gold was invariably observed alongside with the production of only traces of the hydroamination product.

Surprisingly, complex 4 turned out instead to be inactive, at least under the reaction conditions reported in Scheme 4. We speculated that the solubility of complex 4 (which becomes dicationic once the chloride ligand is removed) is limited in the neat reagents, and consequently we repeated the test using as solvent the ionic liquid N-butyl-N'-methylimidazolium triflimidate [bmim]NTf2. However, also in this solvent the activity remained low TOF (TOF $^{t=2h}$  3  $h^{-1}$ ); a lower activity of complex 4 compared to 3 was in any case expected, since the cationic character of the phosphane and the direct P—N bond present in it render ligand  $\mathbf{2}$  less electron-donating than ligand 1, and consequently less able to promote the rate determining step of the hydroamination process, which according to the current knowledge is the protodeauration step liberating the product after nucleophilic attack by the amine to the  $\pi$ -coordinated alkyne [31]. On the other hand, it is interesting to remark that the yield in the reaction with complex 4 appears to grow constantly with time, which indicates a good stability of the catalytically competent species even at longer reaction times.

The two complexes were also employed as catalysts in another technologically relevant hydrofunctionalization reaction, namely the hydroarylation of alkynes [36]. Gold(I) complexes in ionic liquids were very recently found to be effective catalysts for this reaction under

Table 1
Main distances and angle in compounds 3, 4a and 4b.

	3	4a	4b
Au1-P1 (Å)	2.2473(5)	2.2301(14)	2.2286(19)
Au1-Cl1 (Å)	2.2755(7)	2.2820(13)	2.275(2)
P1-Au1-Cl1	178.80(3)°	173.82(5)°	173.25(8)°

#### Table 2

Crystallographic and refinement data for compounds 3, 4a and 4b.

Compound	3	4a	4b
Empirical formula	C33H49AuClN2P	$C_{15}H_{23}AuClF_3N_3O_3PS$	$C_{17}H_{26}AuClF_3N_4O_3PS$
Formula weight	737.13	645.81	686.86
Temperature/K	301(2)	293.8(3)	296.4(3)
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /n	P-1	<i>P</i> 2 <sub>1</sub> /n
a/Å	10.0987(3)	7.8200(4)	7.6524(3)
b/Å	24.0350(6)	12.2436(8)	24.6403(11)
c/Å	13.5809(4)	12.3099(9)	13.3334(8)
$\alpha/^{\circ}$	90	99.752(6)	90
β/°	107.367(3)	102.177(5)	102.703(5)
γ/°	90	96.831(5)	90
Volume/Å <sup>3</sup>	3146.11(16)	1120.72(12)	2452.6(2)
Z	4	2	4
F(000)	1488.0	624.0	1336.0
Crystal size/ mm <sup>3</sup>	$0.2\times0.2\times0.2$	$0.8\times0.04\times0.01$	$0.4\times0.21\times0.08$
Radiation	ΜοΚα (λ = 0.71073)	MoKa ( $\lambda = 0.71073$ )	MoKa ( $\lambda = 0.71073$ )
2⊖ range for data collection/°	4.554 to 65.522	5.326 to 58.652	5.664 to 52.738
Reflections collected	40,887	12,845	24,481
Independent reflections	10,714	5245	4972
Data/restraints/ parameters	10714/0/347	5245/18/259	4972/53/287
Goodness-of-fit on F <sup>2</sup>	1.090	1.005	1.093
Final R indexes	$R_1 = 0.0293,$	$R_1 = 0.0367, wR_2 =$	$R_1 = 0.0592, wR_2 =$
[I>=2σ (I)]	$wR_2 = 0.0608$	0.0608	0.1511
Final R indexes	$R_1 = 0.0371,$	$R_1 = 0.0553, wR_2 =$	$R_1 = 0.0713, wR_2 =$
[all data]	$wR_2 = 0.0634$	0.0698	0.1610
Largest diff. peak/hole / e Å <sup>-3</sup>	0.92/-1.43	0.71/-1.18	1.94/-2.89

neutral conditions [37]. Preliminary tests run using ethyl propriolate and mesitylene as reagents (Scheme 5) with catalysts **3** and **4** evidence, in contrast to hydroamination, the complete inactivity of complex **3** for the reaction. This lack of activity of complex **3** is quite unexpected, since several other gold phosphane complexes, with weaker as well as stronger electron-donating character, all display activity under the employed reaction conditions [37]; the steric bulk of ligand **1**, estimated upon determining its Buried Volume (43.7%) [38], is also not significantly larger than that of other successfully employed ligands [37]. At the moment, we cannot provide an explanation for the observed inactivity of complex **3**. Complex **4** displays instead reasonable activity: the results are reported in Table **4**.

According to the current mechanistic understanding of this reaction, less electron donating ligands at gold should result in more efficient



Scheme 4. Gold catalyzed alkyne hydroamination investigated in this work.

Table 3			
Catalytic performance of complexes	3 and 4	in alkyne h	vdroaminatio

Entry	Catalyst	Time (h)	Alkyne conv. (%)	Yield (%)	TON
1	3	2	14	14	35
		4	24	24	60
2	4	2	0	0	0
3	<b>4</b> <sup>a</sup>	2	3	3	7
		4	5	5	12
		24	30	26	65

<sup>a</sup> Reaction using the ionic liquid [bmim]NTf<sub>2</sub> as solvent.

catalysis, since the rate determining step of the reaction is in this case the external nucleophilic attack by the arene at the alkyne  $\pi$ -coordinated to gold [31]. Ligand 2 is expected to be less electron donating than ligand 1 in consideration of its cationic nature and direct P-N bond, and also features a smaller steric bulk (Buried Volume 39.9%) hence it is not surprising that complex 4 displays a higher catalytic activity than complex 3. On the other hand, albeit catalyst 4 reaches similar TON values compared to other gold-phosphane complexes reported in the literature, its catalytic activity turns out to be somewhat lower under the same reaction conditions (TOF $^{t=1h}$  70 h $^{-1}$  vs. 100–200 h $^{-1}$ ) [37] and the chemoselectivity towards the monosubstituted hydroarylation product at complete alkyne conversion is also lower. Nevertheless, it seems from the data in Table 2 that complex 4 is not rapidly deactivated under reaction conditions, which may lend hope for a further improvement of the efficiency of this catalytic system, for example by optimizing the ligand substituents.

#### 3. Conclusions

Ligands 1 and 2 readily form the corresponding mononuclear gold(I) complexes 3 and 4. The resulting complexes display the expected reactivity as catalysts in alkyne hydrofunctionalization reactions, with the exception of complex 3 in the hydroarylation of ethyl propiolate with mesitylene. Complex 3 also undergoes oxidative addition to the corresponding gold(III) compound in the presence of biphenylene, albeit in low yield, which demonstrates the potential usefulness of the pendant amino group in stabilizing by coordination the oxidative addition product. Finally, complex 4 does not seem to allow deprotonation of position 3 of the ligand heterocycle with formation of a free carbene; more work is needed here to individuate potential reaction partners and



Scheme 3. Oxidative addition of biphenylene to produce 5 and ESI-MS spectrum of the reaction mixture with the product signal at *m*/*z* 853.33.



Scheme 5. Gold catalyzed alkyne hydroarylation investigated in this work.

conditions to indeed demonstrate the feasibility of such a deprotonation.

#### 4. Experimental section

All manipulations were performed using standard Schlenk techniques under an atmosphere of dry argon. Reagents and solvents were commercially available as high-purity products and generally used as received. The ligands **1** [16] and **2** [21] were prepared according to the literature. A Bruker DRX 300 MHz (300.1 MHz for <sup>1</sup>H; 121 MHz for <sup>31</sup>P; 75.5 MHz for <sup>13</sup>C) was used for NMR experiments at 25 °C; chemical shifts ( $\delta$ ) are reported in units of parts per million (ppm) relative to the residual solvent signals. ESI mass spectra were obtained by using a Finnigan Thermo LCQ-Duo ESI mass spectrometer. Elemental analyses were performed with a Thermo Scientific FLASH 2000 instrument at the Department of Chemical Sciences of the University of Padova.

#### 4.1. Synthesis of complex 3

In a three-necked, round bottomed flask were added under an inert atmosphere ligand **1** (172 mg, 0.34 mmol) the gold(I) precursor [AuCl (SMe<sub>2</sub>)] (100 mg, 0.34 mmol) and anhydrous dichloromethane (10 mL). The reaction mixture was left under stirring overnight in the dark. The solvent was subsequently evaporated to dryness and the resulting solid was recrystallized from chloroform/ether. Yield 174 mg (69.6%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.20 (d, *J* = 6.9 Hz, 12H, CH<sub>3</sub>), 1.77 (bs, 12H, Ad), 2.07 (bs, 6H, Ad), 2.27 (m, 6H, Ad), 2.42 (m, 6H, Ad), 4.45 (sept, *J* = 6.9 Hz, 2H, CH), 6.83 (d, *J* = 7.5 Hz, 2H, Ph), 7.06 (t, *J* = 7.5 Hz, 1H, Ph), 7.35 (t, *J* = 7.8 Hz, 2H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 75.25. <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 24.0 (s, CH<sub>3</sub>), 28.9 (d, *J* = 10 Hz, CH<sub>2</sub>), 36.7 (d, *J* = 1.2 Hz, CH<sub>2</sub>), 41.8 (d, *J* = 1.1 Hz, CH), 44.3 (d, *J* = 21 Hz, C), 52.4 (d, *J* = 4.3 Hz, CH), 119.0 (s, CH), 123.2 (s, CH), 130.0 (s, CH), 149.5 (d, *J* = 13 Hz, *ipso*-C), 155.7 (d, *J* = 82 Hz, C=N). Elemental analysis calcd. for C<sub>33</sub>H<sub>49</sub>N<sub>2</sub>PClAu: C 53.77%, H 6.70% N 3.80%; found: C 53.49%, H 6.60%, N 3.75%. ESI-MS (positive ions, CHCl<sub>3</sub>): *m/z* 1437.28 [2 M-Cl<sup>-</sup>], 1495.24 [2 M + Na<sup>+</sup>].

#### 4.2. Synthesis of complex 4

In a three-necked, round bottomed flask were added under an inert atmosphere ligand **2** (140 mg, 0.34 mmol) the gold(I) precursor [AuCl (SMe<sub>2</sub>)] (101 mg, 0.34 mmol) and anhydrous dichloromethane (10 mL). The reaction mixture was left under stirring overnight in the dark. The solvent was subsequently evaporated to dryness and the resulting solid was recrystallized from acetonitrile/ether. Yield 150 mg (68.3%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 1.53 (d, J = 18 Hz 18H, CH<sub>3</sub>), 7.83 (t, J = 6.9 Hz 1H, CH), 8.44 (m, 1H, CH), 8.92 (d, J = 6.7 Hz 1H, CH), 9.16 (d, J =

Table 4	
Catalytic performance of complex 4 in alkyne hydroaryl	ation

Time(h)	Alkyne conv. (%)	TON	Selectiv	Selectivity (%)	
			6	7	8
1	35	70	66	22	12
3	62	124	61	22	17
17	>99	200	42	23	35

9.4 Hz 1H, CH), 9.48 (d, 1H, CH). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$  = 121.98. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$  = 29.0 (d, *J* = 7.2 Hz CH<sub>3</sub>), 42.7 (d, *J* = 19 Hz, C), 113.8 (d, *J* = 4.5 Hz, CH), 121.8 (CH), 130.6 (CH), 140.26 (d, *J* = 3.6 Hz, C), 143.01 (CH). Elemental analysis calcd. for C<sub>15</sub>H<sub>23</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>3</sub>P-SAu: C 27.90%, H 3.59% N 6.51%, S 4.97%; found: C 28.14%, H 3.46%, N 6.36%, S 5.18%. ESI-MS (positive ions, CD<sub>3</sub>CN): *m/z* 496.01 [M–OTf], 609.94 [M–Cl<sup>-</sup>], 1145.65 [2 M–OTf].

#### 4.3. Oxidative addition of biphenylene to complex 3

The procedure was carried out according to [15]. In a Schlenk tube AgSbF<sub>6</sub> (7.9 mg, 23 mmol) was dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.3 mL). In a small round bottomed flask were added under an inert atmosphere complex **3** (17 mg, 23 mmol), biphenylene (35 mg, 0.23 mmol) and CD<sub>2</sub>Cl<sub>2</sub> (0.3 mL). The Schlenk tube was subsequently placed in an ethanol/liquid N<sub>2</sub> bath at -80 °C and the solution in the round bottomed flask was transferred into the Schlenk tube under an inert atmosphere. The reaction mixture was left under stirring at -80 °C for 30 min and was then allowed to warm up to room temperature and left under stirring for 1 additional hour. A sample of the reaction solution was then directly analyzed by NMR and ESI-MS.

#### 4.4. Hydroamination tests

General procedure. In a Schlenk tube equipped with a magnetic stirring bar were placed 20  $\mu$ mol Au complex and 20  $\mu$ mol AgSbF<sub>6</sub>. The tube was degassed and put under an inert atmosphere. 0.70 mL (5.0 mmol) mesitylamine and 0.55 mL (5.0 mmol) phenylacetylene were then injected into the Schlenk tube. The flask was immediately placed in an oil bath preheated at 40 °C and the reaction mixture was vigorously stirred for 4 h. Conversions and yields were determined by <sup>1</sup>H NMR on 0.1 mL samples of the reaction mixture diluted in CDCl<sub>3</sub>.

#### 4.5. Hydroarylation tests

General procedure. Mesitylene (0.35 mL, 2.3 mmol), the gold(I) complex (12.5 µmol), AgSbF<sub>6</sub> (4.6 mg, 13.4 µmol) and the ionic liquid 1-butyl-3-metylimidazolium bis(trifluoromethansulfonyl)imide (0.75 mL, 2.6 mmol) were placed in a Schlenk tube previously evacuated and filled with argon and stirred at room temperature for 5 min. Ethyl propiolate (0.24 mL, 2.3 mmol) was subsequently added and the Schlenk tube was immediately placed in an oil bath thermostated at 40 °C and vigorously stirred at 40 °C for 24 h. Portions of the solution (0.1 mL) were drawn off from the reaction mixture at intervals and analyzed by <sup>1</sup>H NMR.

#### 4.6. X-ray crystal structure determination

Data for compounds 3, 4a, and 4b were collected using an Oxford Diffraction Gemini E diffractometer, equipped with a 2 K  $\times$  2 K EOS CCD area detector and sealed-tube Enhance (Mo) and (Cu) X-ray sources. Single crystals of the compounds were fastened on the top of a Lindemann glass capillary. Data were collected by means of the ω-scans technique using graphite-monochromated radiation and Mo K $\alpha$  ( $\lambda$  = 0.71073) radiation. Detector distance was set at 45 mm. The diffraction intensities were corrected for Lorentz/polarization effects as well as with respect to absorption. Empirical multi-scan absorption corrections using equivalent reflections were performed with the scaling algorithm SCALE3 ABSPACK. Data reduction, finalization and cell refinement were carried out through the CrysAlisPro software. Accurate unit cell parameters were obtained by least squares refinement of the angular settings of strongest reflections, chosen from the whole experiment. The structures were solved with Olex2 [39] by using ShelXT [40] structure solution program by Intrinsic Phasing and refined with the ShelXL [41] refinement package using least-squares minimization. In the last cycles of refinement, non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and a riding

model was used for their refinement. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2040683–2040685).

#### CRediT authorship contribution statement

Andrea Biffis: Conceptualization, Methodology, Validation, Resources, Supervision, Project administration. Marco Baron: Investigation, Validation. Cristina Tubaro: Validation. Marzio Rancan: Investigation, Validation. Lidia Armelao: Resources. Anatoliy Marchenko: Conceptualization. Georgyi Koidan: Investigation, Validation. Anastasiia N. Hurieva: Investigation, Validation. Aleksandr Kostyuk: Conceptualization, Methodology, Validation, Resources, Supervision, Project administration.

#### **Declaration of Competing Interest**

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

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#### References

- [1] C.S. Slone, D.A. Weinberger, C.A. Mirkin, The Transition Metal Coordination Chemistry of Hemilabile Ligands, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2007, pp. 233–350, 10.1002/9780470166499.ch3.
- [2] P. Braunstein, F. Naud, Hemilability of Hybrid Ligands and the Coordination Chemistry of Oxazoline-Based Systems, Angew. Chem. Int. Ed. 40 (2001) 680–699, https://doi.org/10.1002/1521-3773(20010216)40:4<680::AID-ANIE6800>3.0. CO;2-0.
- [3] W.-H. Zhang, S.W. Chien, T.S.A. Hor, Recent advances in metal catalysts with hybrid ligands, Coord. Chem. Rev. 255 (17–18) (2011) 1991–2024, https://doi. org/10.1016/j.ccr.2011.05.018.
- [4] R. Kumar, C. Nevado, Cyclometalated Gold(III) Complexes: Synthesis, Reactivity, and Physicochemical Properties, Angew. Chem. Int. Ed. 56 (8) (2017) 1994–2015, https://doi.org/10.1002/anie.201607225.
- [5] D. Eppel, M. Rudolph, F. Rominger, A.S.K. Hashmi, Mercury-Free Synthesis of Pincer [C'N°C]Au<sup>III</sup> Complexes by an Oxidative Addition/CH Activation Cascade, ChemSusChem 13 (8) (2020) 1986–1990, https://doi.org/10.1002/ cssc.202000310.
- [6] R. Visbal, M.C. Gimeno, N-heterocyclic carbene metal complexes: photoluminescence and applications, Chem. Soc. Rev. 43 (10) (2014) 3551–3574, https://doi.org/10.1039/C3CS60466G.
- [7] V.J. Catalano, A.L. Moore, J. Shearer, J. Kim, Luminescent Copper(I) Halide Butterfly Dimers Coordinated to [Au(CH<sub>3</sub>imCH<sub>2</sub>py)<sub>2</sub>]BF<sub>4</sub> and [Au (CH<sub>3</sub>imCH<sub>2</sub>quin)<sub>2</sub>]BF<sub>4</sub>, Inorg. Chem. 48 (23) (2009) 11362–11375, https://doi. org/10.1021/ic901914n.
- [8] C.E. Strasser, V.J. Catalano, Luminescent Copper(I) Halide Adducts of [Au(im (CH<sub>2</sub>py)<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> Exhibiting Short Au(I)…Cu(I) Separations and Unusual Semibridging NHC Ligands, Inorg. Chem. 50 (21) (2011) 11228–11234, https://doi.org/10.1021/ic201795b.
- [9] P. Ai, M. Mauro, L. DeCola, A.A. Danopoulos, P. Braunstein, A Bis(Diphosphanyl N-Heterocyclic Carbene) Gold Complex: A Synthon for Luminescent Rigid AuAg<sub>2</sub> Arrays and Au<sub>5</sub> and Cu<sub>6</sub> Double Arrays, Angew. Chem. Int. Ed. 55 (10) (2016) 3338–3341, https://doi.org/10.1002/anie.201510150.
- [10] C. Hahn, L. Cruz, A. Villalobos, L. Garza, S. Adeosun, Synthesis, structure and catalytic activity of a gold(1) complex containing 1,2-bis(diphenylphosphino)benzene monoxide, Dalton Trans. 43 (2014) 16300–16309, https://doi.org/10.1039/ C4DT02116A.
- [11] Y. Wang, Z. Wang, Y. Li, G. Wu, Z. Cao, L. Zhang, A general ligand design for gold catalysis allowing ligand-directed anti-nucleophilic attack of alkynes, Nat Commun 5 (1) (2014), 3470, https://doi.org/10.1038/ncomms4470.
- [12] T. Li, Y. Yang, B. Luo, B.o. Li, L. Zong, W. Kong, H. Yang, X. Cheng, L. Zhang, A Bifunctional Ligand Enables Gold-Catalyzed Hydroarylation of Terminal Alkynes under Soft Reaction Conditions, Org. Lett. 22 (15) (2020) 6045–6049, https://doi. org/10.1021/acs.orglett.0c02130.s001.
- [13] L. Huang, F. Rominger, M. Rudolph, A.S.K. Hashmi, A general access to organogold (III) complexes by oxidative addition of diazonium salts, Chem. Commun. 52 (2016) 6435–6438, https://doi.org/10.1039/C6CC02199A.

- [14] L. Huang, M. Rudolph, F. Rominger, A.S.K. Hashmi, Photosensitizer-Free Visible-Light-Mediated Gold-Catalyzed 1,2-Difunctionalization of Alkynes, Angew. Chem. Int. Ed. 55 (15) (2016) 4808–4813, https://doi.org/10.1002/anie.201511487.
- [15] A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, Rational development of catalytic Au(I)/Au(III) arylation involving mild oxidative addition of aryl halides, Nat Commun 8 (1) (2017), 565, https://doi.org/10.1038/ s41467-017-00672-8.
- [16] A. Marchenko, G. Koidan, A. Hurieva, A. Kostyuk, D. Franco, M. Baron, A. Biffis, Pd<sup>II</sup> Complexes with N-(Diadamantylphosphanyl)diaminocarbene and Related Ligands: Synthesis and Catalytic Applications in Intermolecular Alkyne Hydroaminations, Eur. J. Inorg. Chem. 2018 (5) (2018) 652–658, https://doi.org/ 10.1002/ejic.201701342.
- [17] V.J. Catalano, S.J. Horner, Luminescent Gold(I) and Silver(I) Complexes of 2-(Diphenylphosphino)-1-methylimidazole (dpim): Characterization of a Three-Coordinate Au(I)–Ag(I) Dimer with a Short Metal–Metal Separation, Inorg. Chem. 42 (2003) 8430–8438, https://doi.org/10.1021/ic030200m.
- [18] C. Khin, A.S.K. Hashmi, F. Rominger, Gold(I) Complexes of P,N Ligands and Their Catalytic Activity, Eur. J. Inorg. Chem. 2010 (7) (2010) 1063–1069, https://doi. org/10.1002/ejic.200900964.
- [19] C. Wetzel, P.C. Kunz, I. Thiel, B. Spingler, Gold(I) Catalysts with Bifunctional P, N Ligands, Inorg. Chem. 50 (16) (2011) 7863–7870, https://doi.org/10.1021/ ic2011259.
- [20] T. vanDijk, S. Burck, A.J. Rosenthal, M. Nieger, A.W. Ehlers, J.C. Slootweg, K. Lammertsma, Synthesis and Coordination Chemistry of Iminophosphanes, Chem. Eur. J. 21 (26) (2015) 9328–9331, https://doi.org/10.1002/ chem.201501126.
- [21] A.P. Marchenko, H.N. Koidan, A.A. Kirilchuk, A.B. Rozhenko, A.A. Yurchenko, A. N. Kostyuk, Investigation of N- and C-Phosphanylation of [1,2,4]Triazolo[4,3-a] pyridines, Heteroatom Chem. 26 (4) (2015) 277–289, https://doi.org/10.1002/ hc.21258.
- [22] X. Wang, Y. Wang, J. Zhang, X. Zhao, Y.e. Liu, The ionic mononuclear and trinuclear Au(I)-complexes ligated by phosphine-functionalized ionic liquids: Synthesis, characterization, and catalysis to hydration of phenylacetylene, J. Organomet. Chem. 762 (2014) 40–47, https://doi.org/10.1016/j. jorganchem.2014.04.005.
- [23] L.D.M. Nicholls, M. Alcarazo, Applications of α-Cationic Phosphines as Ancillary Ligands in Homogeneous Catalysis, Chem. Lett. 48 (1) (2019) 1–13, https://doi. org/10.1246/cl.180810.
- [24] H. Tinnermann, L.D.M. Nicholls, T. Johannsen, C. Wille, C. Golz, R. Goddard, M. Alcarazo, N -Arylpyridiniophosphines: Synthesis, Structure, and Applications in Au(I) Catalysis, ACS Catal. 8 (11) (2018) 10457–10463, https://doi.org/10.1021/ acscatal.8b03271.s012.
- [25] S. Gaillard, A.M.Z. Slawin, A.T. Bonura, E.D. Stevens, S.P. Nolan, Synthetic and Structural Studies of [AuCl<sub>3</sub>(NHC)] Complexes, Organometallics 29 (2) (2010) 394–402, https://doi.org/10.1021/om900814e.
- [26] M. Baron, C. Tubaro, M. Basato, A.A. Isse, A. Gennaro, L. Cavallo, C. Graiff, A. Dolmella, L. Falivene, L. Caporaso, Insights into the Halogen Oxidative Addition Reaction to Dinuclear Gold(I) Di(NHC) Complexes, Chem. Eur. J. 22 (29) (2016) 10211–10224, https://doi.org/10.1002/chem.201600654.
- [27] F.D. Toste, V. Michelet (Eds.), Gold Catalysis: An Homogeneous Approach; Catalytic Science Series, Imperial College Press, London, UK, 2014.
- [28] D. Pflästerer, A.S.K. Hashmi, Gold catalysis in total synthesis recent achievements, Chem. Soc. Rev. 45 (5) (2016) 1331–1367, https://doi.org/ 10.1039/C5CS00721F.
- [29] R. Dorel, A.M. Echavarren, Gold(I)-Catalyzed Activation of Alkynes for the Construction of Molecular Complexity, Chem. Rev. 115 (17) (2015) 9028–9072, https://doi.org/10.1021/cr500691k.
- [30] L. Huang, M. Arndt, K. Gooßen, H. Heydt, L.J. Gooßen, Late Transition Metal-Catalyzed Hydroamination and Hydroamidation, Chem. Rev. 115 (7) (2015) 2596–2697, https://doi.org/10.1021/cr300389u.
- [31] C.H. Leung, M. Baron, A. Biffis, Gold-Catalyzed Intermolecular Alkyne Hydrofunctionalizations - Mechanistic Insights, Catalysts 10 (2020) 1210, https:// doi.org/10.3390/catal10101210.
- [32] M. Baron, E. Battistel, C. Tubaro, A. Biffis, L. Armelao, M. Rancan, C. Graiff, Single-Step Synthesis of Dinuclear Neutral Gold(I) Complexes with Bridging Di(N-heterocyclic carbene) Ligands and Their Catalytic Performance in Cross Coupling Reactions and Alkyne Hydroamination, Organometallics 37 (22) (2018) 4213–4223, https://doi.org/10.1021/acs.organomet.8b00531.s001.
- [33] D. Malhotra, M.S. Mashuta, G.B. Hammond, B. Xu, A Highly Efficient and Broadly Applicable Cationic Gold Catalyst, Angew. Chem. Int. Ed. 53 (17) (2014) 4456–4459, https://doi.org/10.1002/anie.201310239.
- [34] V. Lavallo, J.H. Wright II, F.S. Tham, S. Quinlivan, Perhalogenated Carba- closo -dodecaborate Anions as Ligand Substituents: Applications in Gold Catalysis, Angew. Chem. Int. Ed. 52 (11) (2013) 3172–3176, https://doi.org/10.1002/ anie.201209107.
- [35] T. Scherpf, C. Schwarz, L.T. Scharf, J.-A. Zur, A. Helbig, V.H. Gessner, Ylide-Functionalized Phosphines: Strong Donor Ligands for Homogeneous Catalysis, Angew. Chem. Int. Ed. 57 (39) (2018) 12859–12864, https://doi.org/10.1002/ anie.201805372.
- [36] V.P. Boyarskiy, D.S. Ryabukhin, N.A. Bokach, A.V. Vasilyev, Alkenylation of Arenes and Heteroarenes with Alkynes, Chem. Rev. 116 (10) (2016) 5894–5986, https://doi.org/10.1021/acs.chemrev.5b00514.
- [37] M. Baron, A. Biffis, Gold(I) Complexes in Ionic Liquids: An Efficient Catalytic System for the C-H Functionalization of Arenes and Heteroarenes under Mild Conditions, Eur. J. Org. Chem. 2019 (22) (2019) 3687–3693, https://doi.org/ 10.1002/ejoc.201900529.

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- [38] L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano, L. Cavallo, Towards the online computer-aided design of catalytic pockets, Nat. Chem. 11 (10) (2019) 872–879, https://doi.org/10.1038/s41557-019-0319-5.
  [39] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2:
- [39] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J Appl Crystallogr. 42 (2009) 339–341, https://doi.org/10.1107/S0021889808042726.
- [40] G.M. Sheldrick, SHELXT Integrated space-group and crystal-structure determination, Acta Crystallogr A Found Adv. 71 (2015) 3–8, https://doi.org/ 10.1107/S2053273314026370.
- [41] G.M. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr C Struct Chem. 71 (2015) 3–8, https://doi.org/10.1107/S2053229614024218.