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Coordination chemistry of gold with *N*-phosphine oxide-substituted imidazolylidenes (POxIms)†

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N-Phosphine oxide-substituted imidazolylidenes (POxIms) have been employed as heteroditopic ligands towards gold centres. Both bis-carbene and mono-carbene gold(I) complexes have been obtained, depending on the steric bulk of the employed POxIm ligand. Oxidation of the gold(I) complexes with halogens or halogen synthons allows access to both bis-carbene and mono-carbene gold(III) complexes, depending on the nature of the starting gold(I) complex and on the oxidation conditions. In all these complexes, the phosphanyl oxide moiety of the ligand is found to not be coordinated by the gold centre, although the crystallographic and spectroscopic characterization of the compounds suggests in most cases the existence of weak electrostatic interactions. A preliminary screening of the complexes as precatalysts in the intermolecular hydroamination of phenylacetylene with mesitylamine has also been carried out.

Introduction

Gold complexes with stable carbene, most notably N-heterocyclic carbene (NHC), ligands represent a class of coordination compounds that has been enjoying steadily growing interest among the scientific community over the last two decades. The main reason for this interest is the stability of the gold–carbene bond,[1] which is the key feature enabling the extensive application of these complexes in several different fields of chemistry. Thus, gold–NHC complexes have been highlighted several times as robust catalysts for diverse chemical reactions.[2–4] They are sufficiently stable to survive for long times in biological media, hence they enable the transport of gold centres inside living cells, where gold can display its bioactivity (*e.g.* as an antitumoral agent).[5,6] Functional gold–NHC complexes as well as polynuclear gold adducts with NHC ligands can be involved in the construction of supramolecular architectures featuring molecular recognition or photophysical properties, thanks, *e.g.*, to the presence of gold–gold closed shell interactions (aurophilic interactions).[7–9] Finally, NHC ligands have been recently highlighted as promising for the derivatization and stabilization of metallic gold surfaces and nanoparticles, including atomically precise gold nanoclusters.[10,11]

On the basis of the above, it is not surprising that a great variety of carbene ligands have been developed, with the scope of producing gold complexes with novel properties. Among this variety, NHC ligands with a tethered additional functionality, potentially able to coordinate metal centres, appear particularly interesting. For example, heteroditopic ligands of this kind have been employed for the production of gold(I) complexes with a strongly distorted coordination geometry, which exhibit peculiar luminescence properties.[12] On the other hand, NHC ligands with an additional pendant functional group can be employed to facilitate unusual oxidative addition reactions to a gold(I) centre forming the corresponding gold(III) complex (as recently highlighted by Bourissou with functional phosphane ligands[13]), or to coordinate additional metal centres, providing access to polymetallic complexes. Finally, these functionalities may also assist the NHC-bound gold centre in performing a catalytic reaction (cooperative catalysis).

We have an ongoing interest in gold–NHC complexes for diverse applications.[14–18] In this contribution, we investigate the coordination chemistry of gold centres with a novel kind of functional NHC ligand, namely *N*-phosphine oxide-substituted imidazolylidenes, alternatively termed POxIms. These carbenes have been originally developed in recent years and employed as organocatalysts by the group of Hoshimoto,[19–21] and we are currently performing a comprehensive investigation on their use as ligands for transition metals. After a first report on the coordination chemistry of palladium(II) with these ligands,[22]

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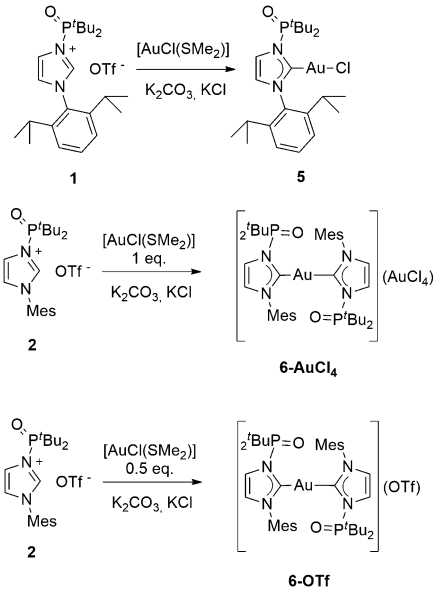
in this contribution, we now turn our attention to complexes of POxIm ligands with gold, and we show that a great variety of complexes with different gold : ligand ratios and different oxidation states for gold are accessible, which in some cases show a remarkable activity as precatalysts in model intermolecular alkyne hydroamination reactions.

Results and discussion

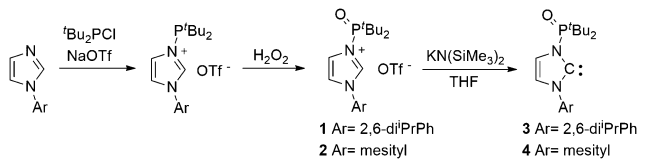
The synthesis of the cationic precursors of POxIm ligands is straightforward (Scheme 1) and follows the route previously developed by Hoshimoto.[19] The resulting *N*-phosphanyl oxide imidazolium precursors **1** and **2** are remarkably stable to air and moisture.

From these precursors, the free POxIms **3** and **4** can be generated by treatment with a base, liberating the carbenes as air-sensitive compounds that can be isolated[19,20] or directly reacted with suitable metal precursors to yield the corresponding complexes.[22] In the context of the preparation of POxIm–Au(I) compounds, though, we have employed another, simpler approach that starts directly from the protonated precursors **1** and **2** and makes use of an inorganic base such as potassium carbonate to deprotonate the imidazolium cation.[18,23,24] Key to success is the formation of ion pairs between the imidazolium cation and an anionic gold(I) polyhalide complex, which facilitates deprotonation with concomitant carbene transfer to gold; consequently, since the imidazolium precursors **1** and **2** do not contain halides as counteranions, we purposely added one equivalent of KCl to the reaction mixture. The aim in our case was to prepare complexes of general stoichiometry POxImAuCl, hence we performed the reaction with a 1 : 1 stoichiometric ratio between the carbene precursor and [AuCl(SMe$_2$)]. Quite surprisingly, this reaction was successful in the case of carbene precursor **1**, yielding complex **5**, whereas it furnished the corresponding cationic dicarbene gold(I) complex cation **6** in the case of precursor **2** (Scheme 2). In the latter case, excess gold undergoes dismutation to gold(0) and gold(III) as $AuCl_4^-$, which produces the complex counteranion in the isolated product (complex **6-AuCl$_4$**); on the other hand, when 0.5 equivalents of [AuCl(SMe$_2$)] was employed, the reaction yielded cleanly the cationic complex with triflate as counteranion (complex **6-OTf**).

We followed by ^{1}H NMR the latter reaction at room temperature: we could monitor the slow conversion of precursor **4** to the cationic biscarbene complex **6**, but no intermediate formation of a monocarbene complex was recorded at any point. Remarkably, attempts to prepare the cationic biscarbene complex with ligand **3** or the neutral monocarbene complex with ligand **4** were unsuccessful. In the former case, either reaction between the carbene precursor with 0.5 equivalents of [AuCl(SMe$_2$)] or reaction of preformed complex **5** with 1 equivalent of the free carbene **3** invariably resulted in the isolation of complex **5** from the reaction mixture. Conversely, reaction between preformed free carbene **4** and [AuCl(SMe$_2$)] in a 1 : 1 ratio invariably led to the formation of the cationic biscarbene complex **6-AuCl$_4$**. Thus, it seems that the different steric bulk of the two carbene ligands determines the different reaction outcome irrespective of the employed synthetic pathway.



Scheme 2 Synthesis of POxIm–gold(I) complexes.



Scheme 1 Synthesis of the POxIm ligands.

Crystals of complex **5** and of the cation **6** could be grown and their structures could be determined. In the case of **6**, slow recrystallization of compound **6-AuCl$_4$** resulted in crystals containing the cation **6** with chloride as counteranion. This is indicative of a certain degree of ligand exchange between gold(I) and gold(III) in solution. Additional evidence of such an exchange stems from the ESI-MS characterization of **6-AuCl$_4$**, in which beside the expected mass peak of **6** at *m*/*z* 889, a second peak at *m*/*z* 959 is also detected, whose mass and isotopic pattern are consistent with $[(\mathbf{4})_2AuCl_2]^+$, *i.e.* a POxIm–gold(III) complex.

The two structures are reported in Fig. 1 and 2. The most interesting aspect of the two structures is the different orientation of the phosphanyl oxide moiety in the two cases; in the case of complex **5**, the P–O bond is turned *anti* to the metal and towards one of the hydrogens of the imidazole backbone, which clearly indicates that there is no interaction between gold and the oxide. On the other hand, complex **6-Cl** is symmetric with a twofold axis passing through the metal atom and with both phosphanyl oxide moieties oriented *syn* to the metal; although there seems to be no proper coordination of the oxide to the metal, the recorded Au–O distance (2.96 Å) is nevertheless significantly shorter than the sum of the van der Waals radii of gold and oxygen (3.18 Å). Thus, there could be a weak electrostatic interaction between the positively charged gold centre and the oxygen of the phosphanyl oxide, which carries a

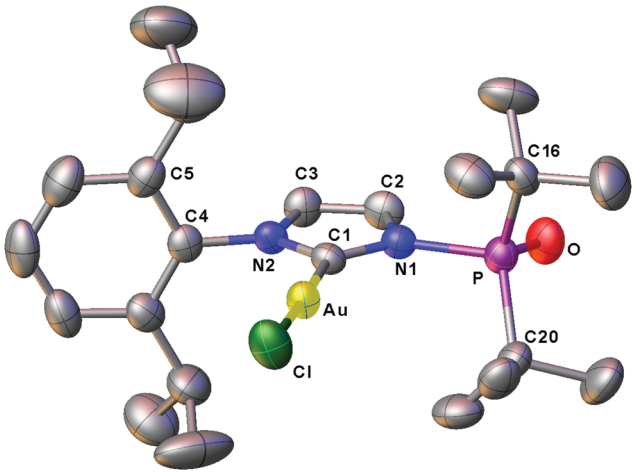


Fig. 1 ORTEP drawing of complex **5**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–Au 1.982(5), Au–Cl1 2.275(1), C1–Au–Cl1 178.01(11).

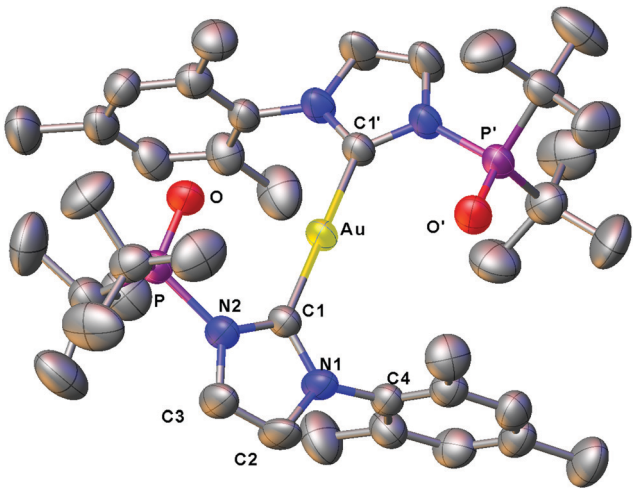


Fig. 2 ORTEP drawing of complex **6-Cl**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the chloride anion have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–Au 2.008(6), O–Au 2.957(6), C1–Au–C1′ 178.9(3). Symmetry operation: ′ = $1 - x, +y, \frac{1}{2} - z$.

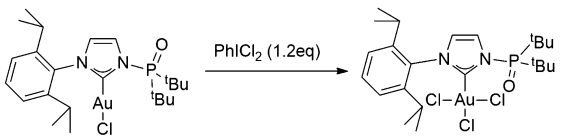
partial negative charge, although the steric bulk of the mesityl group of the second POxIm ligand also favours an orientation of the phosphanyl oxide group with the less sterically demanding P=O bond instead of the *t*-butyl groups pointing towards gold. The chlorine atom is disordered in two positions around a twofold axis and is not involved in interactions.

The difference between the two compounds is much more apparent in solution. The ^{1}H NMR spectrum of **5** is simple and shows the expected features but a strong difference in the chemical shift of the backbone hydrogens of the imidazole ring: the hydrogen in 5-position (H5) resonates at 7.15 ppm whereas the one in 4-position (H4) is considerably deshielded and is found at 8.02 ppm ($\Delta\delta$ = 0.87 ppm). This difference is much greater than that previously recorded for palladium(II) complexes with the same ligand, in which the P–O bond is invariably oriented towards the metal ($\Delta\delta$ = *ca.* 0.3 ppm).[22,25] A similar observation was previously made by the group of Hoshimoto upon comparing the ^{1}H NMR spectra of cationic POxIm precursors **1** and **2** ($\Delta\delta$ = *ca.* 0.7 ppm) with that of free carbenes **3** and **4** ($\Delta\delta$ = *ca.* 1.5 ppm).[19] Again, the chemical shift difference correlated with the recorded orientation of the P–O bond in the crystal structure of the compounds, which pointed towards H4 in the free carbenes and away from it in the precursors. We tend to attribute the large chemical shift difference observed with compounds **3**, **4** and **5** to the existence of an intramolecular attractive interaction between H4 and the phosphanyl oxide group (which is an excellent hydrogen bond acceptor),[26] and to take this chemical shift difference as proof of the *syn*/*anti* orientation of the phosphanyl oxide group with respect to the metal in POxIm complexes in solution.

An indirect confirmation of our assumption comes from the NMR characterization of cation **6**, which presents more complex features than those of **5**. Indeed, two sets of signals in a 1 : 1 ratio are observed in the ^{1}H, ^{13}C and ^{31}P NMR spectra of **6** in CD_3CN, differing in particular in the chemical shifts of the H4 and H5 resonances; this is consistent with the two POxIm ligands in **6** possessing a different conformation in solution, one with the P–O bond *syn* to gold ($\Delta\delta$ = 0.25 ppm) and the other one *anti* to it ($\Delta\delta$ = 0.56 ppm); a complete attribution of the signals to each set was possible through 2D-NMR experiments (see Fig. S11 in the ESI†). Interestingly, the chemical shift values of the various signals depend significantly on the nature of the counteranion of **6** and of the solvent, to the point that in the case of **6-AuCl$_4$** in $CDCl_3$, they coalesce to a single set of signals with large chemical shift differences between H4 and H5 ($\Delta\delta$ = 0.93 ppm); this is indicative of the fact that under these conditions, the two P–O bonds in **6** present an all-*anti* conformation.

We subsequently turned to the preparation of gold(III) complexes with the same ligands, using the well established gold(I) oxidation strategy with elemental halogens or halogen synthons, which previously proved useful with several NHC–gold compounds.[14] Indeed, oxidation of compound **5** with $PhICl_2$[27] cleanly led to the corresponding POxIm–gold(III) trichloride complex **7**, as outlined in Scheme 3.

The crystal structure of complex **7** (Fig. 3) was determined and exhibited the expected features, namely a slightly longer Au–C bond (2.012(3) Å) compared to the corresponding gold(I) complex **5** (1.982(5) Å),[28] and a longer Au–Cl bond for the chloride ligand *trans* to the carbene (Cl3–Au1 2.311(1) Å),



Scheme 3 Preparation of POxIm–gold trichloride **7** by oxidation of the gold(I) precursor **5**.

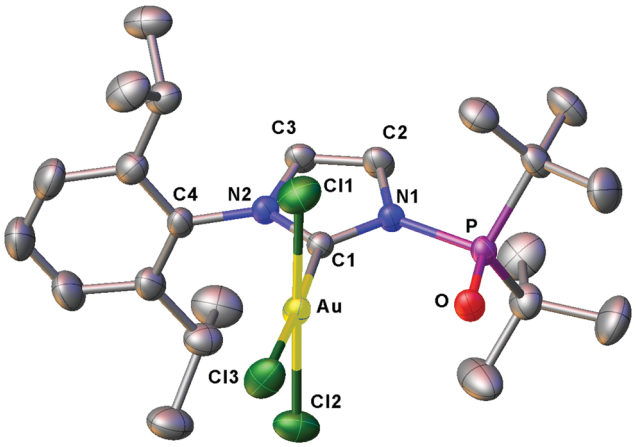
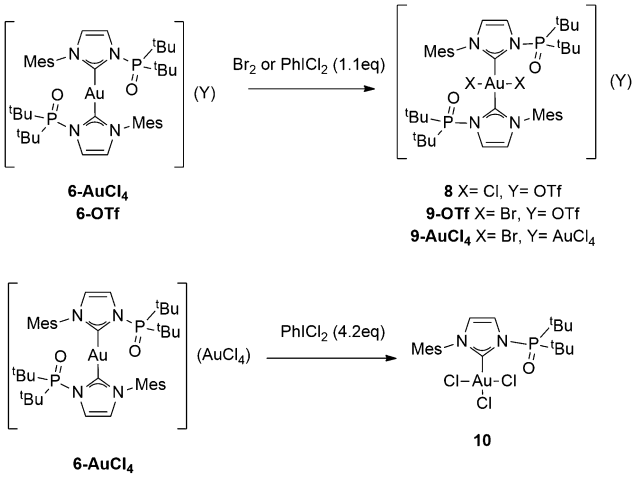


Fig. 3 ORTEP drawing of complex **7**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–Au 2.012(3), Cl3–Au 2.311(1), Cl2–Au 2.281(1), Cl1–Au 2.283(1); Cl1–Au–Cl2 179.02(4), C1–Au–Cl3 175.86(9).

due to the strong *trans* influence of the carbene ligand. On the other hand, in contrast to **5**, the P–O bond in **7** takes up a *syn* conformation to gold; the oxygen distance to gold is found to be 2.949(2) Å in length, which is very close to the Au–O distance in the related gold(I) cation **6** and is again shorter than the sum of the van der Waals radii of Au and O. The ^{1}H NMR characterization of the complex indicates that this conformation is maintained also in solution, as the signals of H4 and H5 are very close ($\Delta\delta$ = 0.01 ppm).

Oxidation of the complex **6-OTf** or **6-AuCl$_4$** led instead to different results depending on the amount and nature of the employed oxidant (Scheme 4). Use of a stoichiometric quantity of $PhICl_2$ or Br_2 produced cleanly the cationic biscarbene complexes **8–9**, whereas use of excess $PhICl_2$ led to the neutral monocarbene complex **10**, a POxIm gold(III) trichloride complex analogous to **7**. Complex **10** was not structurally characterized (see below), but its spectral features closely resemble those of the analogous complex **7**, including the small separation of the



Scheme 4 Preparation of gold(III) complexes with POxIm ligand **4**.

H4 and H5 signals in the ^{1}H NMR spectrum ($\Delta\delta$ = 0.19 ppm), which suggests a *syn* conformation in solution.

The spectral features of complexes **8–9** were instead notably simpler than those of the parent gold(I) cationic complex **6**. In particular, in the ^{1}H NMR spectrum, only one set of signals was invariably present, and the separation of the H4 and H5 signals ($\Delta\delta$ = 0.34 ppm for **8**, 0.17 ppm for **9**) was in all cases compatible with an all-*syn* conformation of the phosphanyl oxide group with respect to gold.

We attempted to grow crystals of all these compounds and were successful in the case of complexes **9-OTf** and **9-AuCl$_4$**. The latter crystals, though, did not contain the expected cationic biscarbene gold(III) dibromide with $AuCl_4^-$ as counteranion, but instead they contained a neutral gold(III) complex (**pseudo-10**), similar in structure to complexes **7** and **10** but with scrambled halide ligands coordinated to the gold centre, which are in part chloride and in part bromide (Fig. 4, atomic occupancies of Cl1/Br1 0.156(4)/0.844(4), Cl2/Br2 0.711(4)/0.289(4), Cl3/Br3 0.187(4)/0.813(4)). Again, formation of such a complex is a further indication of ligand exchange in solution between the cation in complex **9** and the $AuCl_4^-$ counteranion. The structure confirms the *syn* orientation of the P–O bond that was assumed for complex **10**, with a Au–O distance of 2.910(3) Å, slightly shorter than in the case of the complexes investigated before.

Finally, the crystal grown from a solution of complex **9-OTf** contained indeed the expected biscarbene gold(III) dibromide cation (Fig. 5). The *syn* conformation of the two phosphanyl oxide moieties was again confirmed, and the Au–O distance was found to be slightly shorter than the previous cases (2.889(3) Å), in line with the higher electrophilicity expected for a monocationic gold(III) centre.

The application of the synthesized complexes as catalysts has been preliminarily evaluated using as a test reaction the hydroamination of phenylacetylene with mesitylamine, which proceeds in a fully Markovnikov fashion under gold catalysis to produce the corresponding imine (Scheme 5).[29,30]

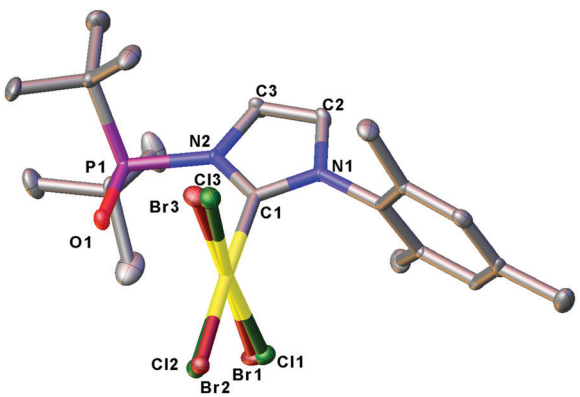


Fig. 4 ORTEP drawing of compound **pseudo-10** that crystallizes out of solutions of complex **9-AuCl$_4$**. Ellipsoids are drawn at the 50% probability level. Solvent molecule and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Au1–C1 2.021(4), Au1–Cl1 2.38(5), Au1–Cl2 2.330(8), Au1–Cl3 2.38(3), Au1–Br1 2.408(3), Au1–Br2 2.422(8), Au1–Br3 2.414(2), O1–Au1 2.910(3), C1–Au1–Br1 89.55(14), C1–Au1–Br2 174.2(2), C1–Au1–Br3 92.16(12), C1–Au1–Cl1 89.2(11), C1–Au1–Cl2 178.2(2), C1–Au1–Cl3 91.6(6).

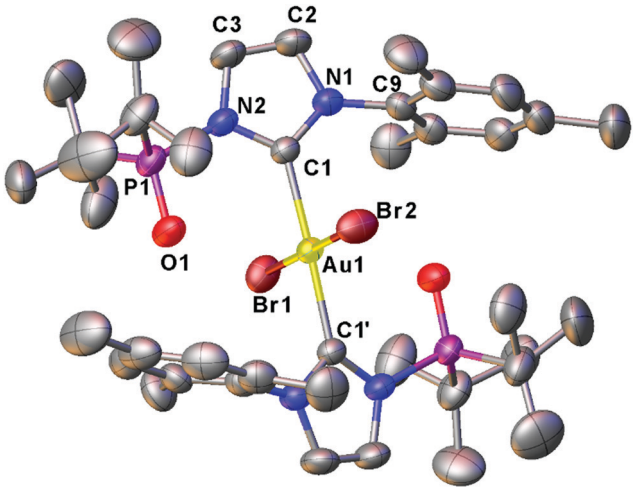
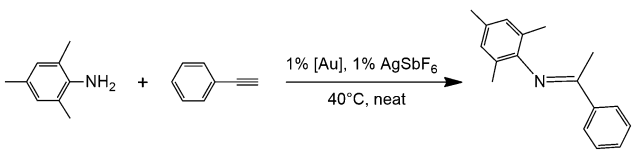


Fig. 5 ORTEP drawing of complex **9-OTf**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Au–C1 2.061(3), Au–Br1 2.4099(8), Au1–Br2 2.4252(8), Br1–Au–Br2 180.0, C1–Au–C1′ 175.67(16), C1–Au–Br1 87.84(8), C1–Au–Br2 92.16(8). Symmetry operation: ′ = $\frac{1}{2} - x, +y, 1 - z$.



Scheme 5 The hydroamination reaction employed in this study.

The corresponding ketone, stemming from the hydrolysis of the initially formed imine by traces of water, is often present as a reaction byproduct. Gold(I) and also gold(III) centres are in general quite efficient in catalysing this reaction, which has often been employed as a standard tool to quantify the reactivity of these complexes.[2,18,30] In this connection, it is important to remark that the pendant phosphanyl oxide moiety could exert a positive role in alkyne hydrofunctionalisation reactions of this kind, as it could interact with the protonated nucleophile activating it and directing its attack to the alkyne π-coordinated to the metal, as suggested for example by C. Hahn *et al.* in the case of a diphosphine monoxide gold(I) complex closely related to some of the complexes reported herein.[31]

Tests were run using neat conditions that we already employed for the evaluation of the catalytic performance of dinuclear gold(I) complexes with di-NHC ligands.[18] One equivalent of $AgSbF_6$ with respect to gold was generally added as a reaction promoter, in order to remove a halide ligand liberating a coordination site on the gold centre for interaction with the reagents; we previously showed that silver salts such as $AgSbF_6$ exhibit *per se* negligible activity in the hydroamination reaction under the employed reaction conditions.[18] We did not test the gold(I) dicarbene cation **6** as a catalyst, since we expected it to be catalytically inactive, given the difficulty in removing an NHC ligand from gold(I). The results are reported in Table 1.

We initially tested the cationic dicarbene gold(III) complex **9-OTf** in the absence of the $AgSbF_6$ promoter, since we wanted

Table 1 Catalytic activity of the complexes in hydroamination

Entry	Catalyst	Time (h)	Hydroamination yield (%)	Hydration yield (%)
1	**5**-$AgSbF_6$	4	66	9
		24	85	15
2	**7**-$AgSbF_6$	4	52	6
		24	71	6
3	**7**-$AgSbF_6$ (3 eq.)	4	57	6
		24	73	6
4	**9-OTf**	4	2	0
		24	3	1
5	**9-OTf**–$AgSbF_6$	4	12	1
		24	13	1
6	**10**-$AgSbF_6$	4	69	11
		24	85	11
7	**10**-$AgSbF_6$ (3 eq.)	4	61	9
		24	65	9
8	IPrAuCl–$AgSbF_6$	4	65	8
		24	86	14

Reaction conditions: 0.983 mmol of phenylacetilene, 0.951 mmol of mesitylamine, 1 mol% gold precatalyst, 1 mol% $AgSbF_6$, 40 °C. Yields determined by ^{1}H-NMR.

to evaluate whether its cationic nature was *per se* sufficient to activate the reagents upon an addition/substitution reaction. However, complex **9-OTf** turned out to be almost completely inactive as a catalyst (entry 4), and even after addition of one equivalent of $AgSbF_6$, its catalytic activity increased only marginally (entry 5). We were quite surprised by this result, but we later found out that the substitution of the bromido ligands in this complex is all but trivial: we checked the reaction of **9-OTf** with one equivalent AgOTf and we were unable to isolate a formally dicationic product stemming from the removal of a bromide ligand by silver, whereas we observed by NMR a mixture of species possibly associated with the coordination of silver to the pendant phosphanyl oxide groups of the complex. In contrast, neutral mono-NHC gold(I) and gold(III) complexes **5**, **7** and **10** were active catalysts for the reaction once activated with one equivalent of $AgSbF_6$ (entries 1, 2 and 6). Addition of excess silver salt (3 equiv.) in the case of gold(III) complexes did not promote further the reaction (entries 3 and 7), which is not surprising since it has been reported that with NHC–Au(III) complexes of this kind, only one halido ligand can be removed by the action of Ag^+.[32] The gold(III) complexes **7** and **10** appear much more active than the related gold(III)–NHC complexes reported by Messerle *et al.* and featuring ligands with pendant pyrazole groups, which provide 61% conversion after 16 hours in the same reaction under much more drastic reaction conditions (100 °C, 2 mol% Au).[33] The catalytic performance of the new gold(I) and gold(III) complexes appears similar and their initial activity is comparable with that of the benchmark commercial gold(I) NHC complex IPrAuCl, which allows a 65% yield to be reached in 4 hours under identical reaction conditions (entry 8). However, the catalytically competent species formed *in situ* upon halide removal do not appear to be exceedingly stable, as the reaction considerably slows down with time and does not reach full conversion of the alkyne (with the only exception of entry 1), even after prolonged reaction times. Consequently, the recorded catalytic efficiency of these complexes does not seem to reach the values recorded

with the most productive gold catalysts reported to date in the literature for this reaction, such as the zwitterionic complex reported by the group of Lavallo, which features a phosphane ligand with a carboranyl substituent and allows full conversions to be reached with as low as 0.001 mol% Au (TONs up to 95 000).[34]

Experimental

Materials and methods

All manipulations of air and moisture sensitive compounds were carried out in a glove box or using standard Schlenk techniques under an atmosphere of argon or dinitrogen. The reagents were purchased from Aldrich as high-purity products and generally used as received. All solvents were purified and dried by standard methods. Ligand precursors **1** and **2**[19] and reagent $PhICl_2$[35] were prepared according to literature procedures. NMR spectra were recorded using a Bruker Avance spectrometer working at 300 MHz (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P); chemical shift (δ) values are reported in units of ppm relative to the residual solvent signals and to external 85% H_3PO_4 (for ^{31}P). ESI-MS analysis was performed using a LCQ-Duo (Thermo-Finnigan) operating in positive ion mode. Instrumental parameters: capillary voltage 10 V; spray voltage 4.5 kV; capillary temperature 200 °C; mass scan range from 150 to 2000 amu; N_2 was used as sheath gas; the He pressure inside the trap was kept constant. The pressure directly read by an ion gauge (in the absence of the N_2 stream) was 1.33×10^{-5} Torr. Sample solutions, prepared by dissolving the compounds in acetonitrile, were directly infused into the ESI source by a syringe pump at 8 μl min^{-1} flow rate. Elemental analysis was carried out using a Fisons EA 1108 CHNS-O instrument or with a Carlo Erba analyzer.

Synthesis of complex 5

0.1004 g (0.1862 mmol) of precursor **1**, 0.0166 g (0.2227 mmol) of KCl, 0.2555 g (1.849 mmol) of K_2CO_3 and 0.0522 g (0.1868 mmol) of [(Me_2S)AuCl] were placed in a round-bottomed flask under Ar. 30.0 ml of dry acetonitrile was then added; the flask was placed in an oil bath thermostated at 60 °C and the reaction mixture was stirred for 3.0 h. The mixture was filtered over Celite and the solids were washed with acetonitrile (3 × 3.0 ml). The solution was evaporated to dryness and the resulting solid was treated with 5.0 ml of chloroform. Undissolved solids were removed by filtration and the solution was finally evaporated to dryness to yield the product as a white solid. Yield 89.6% (0.1036 g). ^{1}H-NMR ($CDCl_3$): δ = 8.01 (m, 1H, H^{im}), 7.50 (t, $^3J_{HH}$ = 7.78 Hz, 1H, H^{aryl}), 7.27 (d, 2H), 7.14 (m, 1H, H^{im}), 2.31 (sept, $^3J_{HH}$ = 7.01 Hz, 2H, CH^{iPr}), 1.57 (d, $^3J_{HP}$ = 15.60 Hz, 18H, $CH_3{}^{tBu}$), 1.32 (d, $^3J_{HH}$ = 6.91 Hz, 6H, $CH_3{}^{iPr}$), 1.13 (d, $^3J_{HH}$ = 6.90 Hz, 6H, $CH_3{}^{iPr}$). ^{13}C-NMR ($CDCl_3$): δ 174.5 (d, J = 8.1 Hz, C^{carb}), 145.4 (s, C^{aryl}), 134.3 (s, C^{aryl}), 131.1 (s, CH^{aryl}), 125.3 (d, J = 3.4 Hz, CH^{im}), 124.5 (s, CH^{aryl}), 122.3 (d, J = 3.9 Hz, CH^{im}), 38.8 (d, J = 62.0 Hz, C^{tBu}), 28.8 (s, CH^{iPr}), 27.5 (s, $CH_3{}^{tBu}$), 24.3 (s, $CH_3{}^{iPr}$). ^{31}P-NMR ($CDCl_3$): δ 72.8 (s). ESI-MS (m/z): 643.35 [75%, $(M + Na)^+$], 1263.05 [100%, $(M_2 + Na)^+$]. Elemental analysis: calcd (%) for $C_{23}H_{37}AuClN_2OP$ (MM 620.68): C 44.49, H 6.01, N 4.51; found: C 44.55, H 6.37, N 4.73.

Synthesis of complex 6-$AuCl_4$

0.2435 g (0.4904 mmol) of precursor **2**, 0.0398 g (0.5338 mmol) of KCl, 0.8272 g (5.6553 mmol) of K_2CO_3 and 0.13976 g (0.5012 mmol) of [(Me_2S)AuCl] were placed in a round-bottomed flask under Ar. 10.0 ml of dry acetonitrile were then added; the flask was placed in an oil bath thermostated at 65 °C and the reaction mixture was stirred for 24 h. The mixture was filtered over Celite and the solids were washed with acetonitrile (3 × 3.0 ml). The solution was evaporated to dryness and the residue was taken up in 10.0 ml of dichloromethane. Undissolved solids were removed by filtration and the solution was finally evaporated to dryness and treated with 10.0 ml of Et_2O to isolate the product as a white solid. Yield 50.6% (0.1524 g). ^{1}H-NMR (CD_3CN): δ = 7.94 (m, 1H, H^{im}), 7.64 (m, 1H, H^{im}), 7.38 (m, 1H, H^{im}), 7.36 (m, 1H, H^{im}), 7.10–7.08 (m, 4H, H^{aryl}), 2.35 (6H, CH_3^{para}), 2.19 (s, 6H, CH_3^{ortho}), 2.00 (s, 6H, CH_3^{ortho}), 1.71 (s, 6H, CH_3^{ortho}), 1.52 (d, $^3J_{HP}$ = 15.96 Hz, 18H, $CH_3{}^{tBu}$), 1.37 (d, $^3J_{HP}$ = 15.46 Hz, 18H, $CH_3{}^{tBu}$). ^{1}H-NMR ($CDCl_3$): δ = 8.01 (m, 2H, H^{im}), 7.08 (m, 2H, H^{im}), 6.99 (s, 4H, H^{aryl}), 2.34 (s, 6H, CH_3^{para}), 2.01 (s, 12H, CH_3^{ortho}), 1.58 (d, $^3J_{HP}$ = 16.08 Hz, 36H, $CH_3{}^{tBu}$). ^{31}P-NMR ($CDCl_3$): δ = 72.70. ^{13}C-NMR ($CDCl_3$): δ = 173.40 (d, $^2J_{CP}$ = 8.16 Hz, C^{carb}), 140.21 (s, C^{aryl}), 134.94 (s, C^{aryl}), 134.38 (s, C^{aryl}), 129.71 (s, CH^{aryl}), 125.58 (d, J = 3.46 Hz, CH^{im}), 121.3 (d, J = 4.13 Hz, CH^{im}), 38.70 (d, $^1J_{CP}$ = 62.01 Hz, C^{tBu}), 27.53 (s, $CH_3{}^{tBu}$), 21.33 (s, CH_3^{para}), 17.87 (s, CH_3^{ortho}). ESI-MS (m/z): 889.38 [100%, $[(M\text{-}AuCl_4)^+]$, 959.30 [45% $(M\text{-}AuCl_2)^+$]]. Elemental analysis: calcd (%) for $C_{40}H_{62}N_4P_2O_2Au_2Cl_4$ (MM 1228.18): C 39.10, H 5.09; N 4.56; found: C 39.32, H 5.40, N 4.28.

Synthesis of complex 6-OTf

0.2004 g (0.4360 mmol) of precursor **2**, 0.01780 g (0.2388 mmol) of KCl, 0.2758 g (0.1996 mmol) of K_2CO_3 and 0.0573 g (0.2050 mmol) of [(Me_2S)AuCl] were placed in a round-bottomed flask under Ar. 10.0 ml of dry acetonitrile was then added; the flask was placed in an oil bath thermostated at 40 °C and the reaction mixture was stirred for 72 h. The mixture was filtered over Celite and the solids were washed with acetonitrile (3 × 3.0 ml). The solution was evaporated to dryness and the residue was taken up in 10.0 ml of dichloromethane. Undissolved solids were removed by filtration and the solution was finally evaporated to dryness and treated with 10.0 ml of Et_2O to isolate the product as a white solid. Yield 75.0% (0.1598 g). ^{1}H-NMR (CD_3CN): δ = 7.87 (m, 1H, H^{im}), 7.60 (m, 1H, H^{im}), 7.35 (m, 1H, H^{im}), 7.31 (m, 1H, H^{im}), 7.00 (m, 4H, H^{aryl}), 2.25 (6H, CH_3^{para}), 1.90 (s, 6H, CH_3^{ortho}), 1.71 (s, 6H, CH_3^{ortho}) 1.32 ppm (d, $^3J_{HP}$ = 15.91 Hz, 18H, $CH_3{}^{tBu}$), 1.24 (d, $^3J_{HP}$ = 15.39 Hz, 18H, $CH_3{}^{tBu}$). ^{31}P-NMR (CD_3CN): δ = 71.05 (1P), 64.07 (1P). ^{13}C-NMR (CD_3CN): δ = 189.76 (d, $^2J_{CP}$ = 8.29 Hz, C^{carb}), 184.74 (d, $^2J_{CP}$ = 8.86 Hz, C^{carb}), 140.84 (s, C^{aryl}), 140.60 (s, C^{aryl}), 136.48 (s, C^{aryl}), 136.17 (s, C^{aryl}), 135.98 (s, C^{aryl}), 135.50 (s, C^{aryl}), 130.13 (s, CH^{aryl}), 130.0 (s, CH^{aryl}), 126.49 (d, J = 3.07 Hz, CH^{im}), 125.31 (d, J = 2.67 Hz, CH^{im}), 123.62 (d, J = 3.40 Hz, CH^{im}), 122.59 (d, J = 3.63 Hz, CH^{im}), 39.37 (d, $^1J_{CP}$ = 11.70 Hz, C^{tBu}), 35.02 (d, $^1J_{CP}$ = 13.00 Hz, C^{tBu}), 27.34 (s, $CH_3{}^{tBu}$), 26.48 (s, $CH_3{}^{tBu}$), 21.07 (s, CH_3^{para}), 17.89 (s, CH_3^{ortho}). ESI-MS (m/z): 889.38 [100% $(M\text{-}OTf)]^+$. Elemental analysis: calcd (%) for $C_{41}H_{62}N_4P_2O_5SF_3Au$ (MM 1038.35): C 47.40, H 6.01, N 5.39, S 3.09; found: C 47.74, H 6.46, N 5.30, S 2.86.

Synthesis of complex 7

0.1016 g (0.1636 mmol) of complex **5** and 0.0579 g (0.1963 mmol) of $PhICl_2$ were placed in a round-bottomed flask under Ar. 10.0 ml of dry acetonitrile was then added and the resulting solution was stirred at room temperature for 5.0 h. All volatiles were subsequently evaporated under vacuum and the resulting yellowish-white solid was extensively washed with diethylether (3 × 10.0 ml). Yield 57.2% (0.0648 g). ^{1}H-NMR (CD_3CN): δ = 7.81–7.80 (m, 2H, H^{im}), 7.63 (t, 1H, $^3J_{HH}$ = 7.81 Hz, H^{aryl}), 7.43 (d, 2H, $^3J_{HH}$ = 7.81 Hz, H^{aryl}), 2.63 (sept, 2H, $^3J_{HH}$ = 6.54 Hz, CH^{iPr}), 1.45 (d, 18H, $^3J_{PH}$ = 16.02 Hz, $CH_3{}^{tBu}$), 1.30 (d, $^3J_{HH}$ = 6.54 Hz, 6H, $CH_3{}^{iPr}$), 1.04 (d, $^3J_{HH}$ = 6.54 Hz, 6H, $CH_3{}^{iPr}$). ^{31}P-NMR (CD_3CN): δ = 73.33. ^{13}C-NMR (CD_3CN): δ = 147.49 (s, CH^{aryl}), 133.91 (s, C^{aryl}), 133.57 (s, CH^{aryl}), 130.26 (d, J = 3.24 Hz, CH^{im}), 125.49 (s, CH^{aryl}), 125.14 (d, J = 3.20 Hz, CH^{im}), 39.41 (d, $^1J_{CP}$ = 61.48 Hz, C^{tBu}), 29.76 (s, CH^{iPr}), 27.15 (s, $CH_3{}^{tBu}$), 26.49 (s, $CH_3{}^{iPr}$), 22.67 (s, $CH_3{}^{iPr}$). ESI-MS (m/z): 728.93 [60% $(M + K)^+$], 1420.76 [100% $(M_2 + K)^+$]. Elemental analysis: calcd (%) for $C_{23}H_{37}N_2POCl_3Au$ (MM 691.59): C 39.93, H 5.39, N 4.05; found: C 39.42, H 5.27, N, 3.97.

Synthesis of complex 8

0.0234 g (0.0225 mmol) of complex **6-OTf** and 0.0076 g (0.0270 mmol) of $PhICl_2$ were placed in a round-bottomed flask under Ar. 5.0 ml of dry acetonitrile was then added and the resulting solution was stirred at room temperature for 5.0 h. All volatiles were subsequently evaporated under vacuum and the resulting yellowish-white solid was extensively washed with diethylether (2 × 2.0 ml). Yield 92.1% (0.0230 g). ^{1}H-NMR (CD_3CN): δ = 7.68 (s, 2H, H^{im}), 7.34 (s, 2H, H^{im}), 6.93 (s, 4H, H^{aryl}), 2.49 (s, 6H, CH_3^{para}), 1.76 (s, 12H, CH_3^{ortho}), 1.41 (d, $^3J_{CP}$ = 15.49 Hz, 36H, $CH_3{}^{tBu}$). ^{31}P-NMR (CD_3CN): δ = 67.70. ^{13}C-NMR (CD_3CN): δ = 158.38 (m, C^{carb}), 140.63 (s, C^{aryl}), 136.13 (s, C^{aryl}), 134.56 (s, C^{aryl}), 130.56 (s, CH^{aryl}), 128.30 (d, J = 2.78 Hz, CH^{im}), 124.75 (d, J = 3.54 Hz, CH^{im}), 39.34 (d, $^1J_{CP}$ = 62.68 Hz, C^{tBu}), 27.12 (s, $CH_3{}^{tBu}$), 21.33 (s, CH_3^{para}), 18.53 (s, CH_3^{ortho}). ESI-MS (m/z): 889.33 [15% $(M\text{-}OTf\text{-}2Cl)^+$], 959.28 [100% $(M\text{-}OTf)^+$]. Elemental analysis: calcd (%) for $C_{41}H_{62}N_4P_2O_5SF_3Cl_2Au$ (MM 1109.26): C 44.37, H 5.63, N 5.05, S 2.89; found: C 44.21, H 5.83, N 4.98, S 2.69.

Synthesis of complex 9-OTf

0.1029 g (0.0990 mmol) of complex **6-OTf** was dissolved in a round-bottomed flask under Ar into 3.0 ml of dry CH_3CN. 0.980 ml (0.099 mmol) of a 0.101 M solution of Br_2 in dry CH_3CN was then added, and the resulting solution was stirred at room temperature for 3.0 h, during which time a white solid precipitated out of the solution. The solution was concentrated under vacuum to about one fifth of its original volume. The solid product was filtered off and washed with Et_2O (2 × 2.0 ml). Yield 70.1% (0.0832 g). ^{1}H-NMR (CD_3CN): δ = 7.63 (m, 2H, H^{im}), 7.45 (s, 2H, H^{im}), 6.96 (s, 4H, H^{aryl}), 2.29 (s, 6H, CH_3^{para}), 2.16 (s, 12H, CH_3^{ortho}), 1.26 (d, $^3J_{CP}$ = 15.66 Hz, 36H, $CH_3{}^{tBu}$). ^{31}P-NMR (CD_3CN): δ = 68.56. ^{13}C-NMR (DMSO-d_6): δ = 154.18 (d, $^2J_{CP}$ = 6.32 Hz, C^{carb}), 138.60 (s, C^{aryl}), 135.29 (s, C^{aryl}), 135.35 (s, C^{aryl}), 128.87 (s, CH^{aryl}), 128.34 (m, CH^{im}), 124.66 (m, CH^{im}), 37.79 (d, $^1J_{CP}$ = 62.60 Hz, C^{tBu}), 26.41 (s, $CH_3{}^{tBu}$), 20.74 (s, CH_3^{para}), 19.17 (s, CH_3^{ortho}). ESI-MS (m/z): 889.35 [60% $(M\text{-}OTf\text{-}2Br)^+$], 1049.16 [100% $(M\text{-}OTf)^+$]. Elemental analysis: calcd (%) for $C_{41}H_{62}N_4P_2O_5SF_3Br_2Au$ (MM 1198.16): C 41.08, H 5.21, N 4.67, S 2.67; found: C 40.91, H 5.58, N 4.67, S 2.42.

Synthesis of complex 9-$AuCl_4$

0.1467 g (0.1194 mmol) of complex **6-$AuCl_4$** was dissolved in a round-bottomed flask under Ar into 5.0 ml of dry CH_3CN. 0.390 ml (0.220 mmol) of a 0.564 M solution of Br_2 in dry CH_3CN was then added, and the resulting solution was stirred at room temperature for 3.0 h, during which time a yellow solid precipitated out of the solution. The solution was concentrated under vacuum to about one fifth of its original volume. The solid product was filtered off and washed with Et_2O (2 × 2.0 ml). Yield 43.4% (0.0956 g). ^{1}H-NMR (CD_3CN): δ = 7.80 (m, 2H, H^{im}), 7.63 (s, 2H, H^{im}), 7.09 (s, 4H, H^{aryl}), 2.36 (s, 6H, CH_3^{para}), 2.21 (s, 12H, CH_3^{ortho}), 1.45 (d, $^3J_{CP}$ = 16.01 Hz, 36H, $CH_3{}^{tBu}$). ^{31}P-NMR (CD_3CN): δ = 73.38. ^{13}C-NMR (DMSO-d_6): δ = 140.21 (s, C^{aryl}), 135.17 (s, C^{aryl}), 135.18 (s, C^{aryl}), 129.39 (s, C^{aryl}), 128.93 (d, J = 3.00 Hz, C^{im}), 124.68 (d, J = 3.38 Hz, C^{im}), 38.21 (d, $^1J_{CP}$ = 61.33 Hz, C^{tBu}), 26.63 (s, $CH_3{}^{tBu}$), 20.60 (s, CH_3^{para}), 19.18 (s, CH_3^{ortho}). ESI-MS (m/z): 889.35 [60% $(M\text{-}OTf\text{-}2Br)^+$], 1049.16 [100% $(M\text{-}OTf)^+$]. Elemental analysis: calcd (%) for $C_{40}H_{62}N_4P_2O_2Br_2Cl_4Au_2$ (MM 1387.99): C 34.60, H 4.50, N 4.04; found: C, 34.54; H, 4.54; N, 3.97.

Synthesis of complex 10

0.0659 g (0.0536 mmol) of complex **6-$AuCl_4$** and 0.0619 g (0.2251 mmol) of $PhICl_2$ were placed in a round-bottomed flask under Ar. 5.0 ml of dry acetonitrile was then added and the resulting solution was stirred at room temperature overnight. All volatiles were subsequently evaporated under vacuum and the resulting yellowish-white solid was extensively washed with diethylether (3 × 3.0 ml). Yield 52.6% (0.0183 g). ^{1}H-NMR (CD_3CN): δ = 7.83 (s, 1H, H^{im}), 7.64 (s, 1H, H^{im}), 7.11 (s, 2H, H^{aryl}), 2.37 (s, 3H, CH_3^{para}), 2.15 (s, 6H, CH_3^{ortho}), 1.43 (d, $^3J_{HP}$ = 15.87 Hz, 18H, $CH_3{}^{tBu}$). ^{31}P-NMR (CD_3CN): δ = 73.00. ^{13}C-NMR (CD_3CN): δ = 142.11 (s, C^{aryl}), 136.82 (s, C^{aryl}), 130.46 (s, C^{aryl}), 128.77 (m, C^{im}), 125.85 (m, C^{im}), 39.33 (d, $^1J_{CP}$ = 61.52 Hz, C^{tBu}), 27.11 (s, $CH_3{}^{tBu}$), 21.16 (s, CH_3^{para}), 18.88 (s, CH_3^{ortho}). ^{13}C-NMR (DMSO-d_6): δ = 140.37 (s, C^{aryl}), 135.32 (s, C^{aryl}), 135.07 (s, C^{aryl}), 129.40 (s, C^{aryl}), 128.49 (m, C^{im}), 125.49 (m, C^{im}), 37.63 (d, C^{tBu}), 26.28 (s, $CH_3{}^{tBu}$), 20.64 (s, CH_3^{para}), 18.13 (s, CH_3^{ortho}). ESI-MS (m/z): 670.89 [60% $(M + Na)^+$], 1322.73 [100% $(M_2 + Na)^+$]. Elemental analysis: calcd (%) for $C_{20}H_{31}N_2POCl_3Au$ (MM 649.54): C 36.97, H 4.81, N 4.31; found: C 36.88, H, 4.70, N 4.48.

Crystallography

The crystallographic data for complexes **5**, **6-Cl** and **7** were obtained by mounting a single crystal on a glass fiber and transferring it to an APEX II Bruker CCD diffractometer. The APEX 3 program package[36] was used to obtain the unit-cell geometrical parameters and for the data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data

were processed using SAINT[37] and SADABS[37] to obtain the data file of the reflections. The structures were solved using SHELXT[38] (Intrinsic Phasing method in the APEX 3 program). The refinement of the structures (based on F^2 by full-matrix least-squares techniques) was carried out using the SHELXTL-2014/7 program[38] in the WinGX suite v.2014.1.[39] The hydrogen atoms were introduced in the refinement in defined geometry and refined ''riding'' on the corresponding carbon atoms.

Data for compound **9-OTf** were collected using an Oxford Diffraction Gemini E diffractometer, equipped with a 2 K × 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. 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.

Data for the crystals derived from complex **9-AuCl$_4$** (Fig. 4) were collected using a single crystal X-ray diffractometer equipped with a CMOS detector (APEX III, κCMOS), a TXS rotating anode with Mo Kα radiation (λ = 0.71073 Å), and a Helios optic using the APEX III software package.[36] The crystals were fixed on the top of a kapton microsampler with perfluorinated ether, transferred to the diffractometer, and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT.[37] Absorption corrections, including odd and even order spherical harmonics, were performed using SADABS.[37] The structures were solved with Olex2[40] by using ShelXT[38] 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.†

Catalytic tests

General procedure: 10 μmol of Au complex and 10–30 μmol of $AgSbF_6$ were placed in a Schlenk tube equipped with a magnetic stirring bar. The tube was degassed and put under an inert atmosphere. 0.11 ml (1.0 mmol) of mesitylamine and 0.14 ml (1.0 mmol) of 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 24 hours. Conversions and yields were determined by ^{1}H NMR on a sample of the reaction mixture diluted in $CDCl_3$, after the addition of 1,4-bis-trimethylsilylbenzene as an internal standard.

Conclusions

In this contribution, we have examined the coordination chemistry of *N*-phosphine oxide-substituted imidazolylidenes (POxIms) as heteroditopic ligands for gold centres. We have shown that it is possible to obtain both bis-carbene and mono-carbene gold(I) complexes, depending on the steric bulk of the employed POxIm ligand. From these complexes, gold(III) complexes can be prepared upon gold(I) oxidation with halogens or halogen synthons. Again, both bis-carbene and mono-carbene gold(III) complexes are accessible, depending on the nature of the starting gold(I) compound and on the oxidation conditions. The complexes were found to undergo ligand exchange relatively easily and to generally present the phosphanyl oxide group uncoordinated to the gold centre, though weak electrostatic interactions between the metal and the phosphanyl oxygen seem to be present in most cases. A preliminary screening of the complexes as precatalysts in the intermolecular hydroamination of phenylacetylene with mesitylamine has showcased the good catalytic performance of the mono-carbene gold(I) and gold(III) complexes, which is comparable to the benchmark IPrAuCl. However, the stability of these catalytic systems seems to be an issue, so that steps will be taken to increase the robustness of these complexes and to exploit the opportunities provided by the pendant phosphanyl oxide group in a cooperative catalytic event with the gold centre. Efforts in these directions are currently underway.

Conflicts of interest

There are no conflicts to declare.

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