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Gold(III) iminophosphorane complexes as catalysts in C–C and C–O bond formations

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ABSTRACT

The reaction of $K[AuCl_4]$ with $AgClO_4$ and iminophosphorane ligands (N,N-IM) $Ph_3P{=}NR$ [R = CH_2-2-NC_5H_4 (**1**), C(O)-2-NC_5H_4 (**2**)] or $Ph_2PyP{=}NR$ [Py = -2-NC_5H_4; R = Ph (**3**), C(O)Ph (**4**)] (mol ratio 1:2.2:1) in acetonitrile affords complexes $[AuCl_2(N,N\text{-}IM)]ClO_4$ (**5–8**). These compounds are air- and moisture-stable and they have been evaluated in two types of catalytic processes. They have been found to be effective catalysts in the addition of 2-methylfuran or azulene to methyl vinyl ketone, as well as in the synthesis of 2,5-disubstituted oxazoles from N-propargylcarboxamides. The reactions proceed in mild conditions and with similar yields to those described for $AuCl_3$. Using this method, oxazoles bearing a thiophene functional group 2-(2′-thienyl)-5-methylthiazole can be prepared in excellent yields. In all cases the intermediate 5-methylene-4,5-dihydroxazole can be observed by ^1H NMR.

1. Introduction

The catalytic functionalizations of C–H bonds under mild conditions are an example of atom economy and, therefore, of environmentally friendly reactions. Much attention has been directed to research in this area during the last ten years [1]. Gold compounds have been successfully applied in C–H functionalization reactions to form C–C and C-heteroatom bonds in the presence of different electrophiles such as alkynes, alkenes or even nitrogen sources [2]. The catalyst of choice for many of these transformations has been the very hygroscopic and acidic $AuCl_3$ salt. We and others have focused in the search for gold(III) compounds as air- and moisture-stable and molecularly well-defined alternatives to $AuCl_3$. In this context it has been reported that gold(III) coordination and organometallic compounds catalyze diverse processes like the addition of nucleophiles to alkynes [3–5], the cycloisomerization of allenones [5], the phenol synthesis [6], the 1,3-dipolar cycloaddition to nitrones [7], or the addition of 2-methylfuran or electron-rich arenes to methyl vinyl ketone [8]. Moreover, the functionalization of ligands bonded to gold(III) centers has allowed for their use in supported catalytic hydrogenations [9], hydrosilylations [10], or C–C bond forming reactions [11] with subsequent recovery of the gold catalysts.

We described recently that gold(III) compounds containing iminophosphorane ligands [8] are efficient catalysts in the addition of 2-methylfuran or electron-rich arenes to methyl vinyl ketone [12]. Cycloaurated derivatives $[Au\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}N(C_6H_4X))\text{-}2\}Cl_2]$ (X = H, Me) resulted as efficient as $AuCl_3$ in these processes and even outperformed this salt in reactions with acid-sensitive electron-rich arenes [8]. From NMR experiments we gathered that the catalytically active species were cationic gold(III) compounds stabilized by the C,N-backbone. However, Au(III) coordination complexes of the type $[AuCl_3\{Ph_3P{=}NC(O)R\}]$, with stabilized iminophosphoranes as monodentate ligands, were not as efficient even in combination with silver salts, and decomposed to metallic gold during the reaction.

In this paper we report on the synthesis of new air- and moisture-stable cationic gold(III) coordination complexes with N,N-chelating iminophosphorane ligands. These compounds resulted as efficient as the previously reported iminophosphorane cycloaurated derivatives in the addition reactions of 2-methylfuran or electron-rich arenes to methylvinylketone. They were also evaluated in the synthesis of 2,5-disubstituted oxazoles, compounds of significant biological activity, from N-propargyl-carboxamides [13]. The $AuCl_3$ methodology has already been used by Merck as a step in the synthesis of a pharmaceutically active substance [14].

2. Results and discussion

2.1. Synthesis of the coordination gold(III) compounds

The reaction of $K[AuCl_4]$ with $AgClO_4$ and iminophosphorane ligands (N,N-IM) $Ph_3P{=}NR$ [R = CH_2-2-NC_5H_4 (**1**), C(O)-2-NC_5H_4 (**2**)] or $Ph_2PyP{=}NR$ [Py = -2-NC_5H_4; R = Ph (**3**), C(O)Ph (**4**)] (mol ratio 1:2.2:1) in acetonitrile at RT afforded complexes $[AuCl_2(N,N\text{-}IM)]ClO_4$ (**5–8**) (Scheme 1). Compounds **5–8** are obtained as air- and moisture-stable yellow solids that are insoluble in chlorinated

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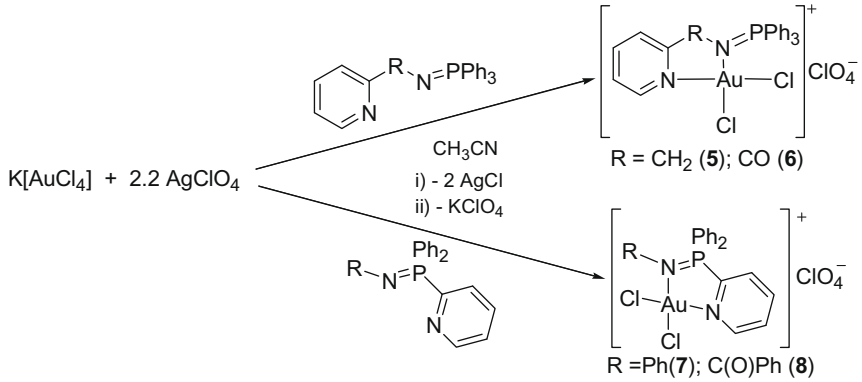


Scheme 1. Syntheses of the gold(III) coordination iminophosphorane complexes.

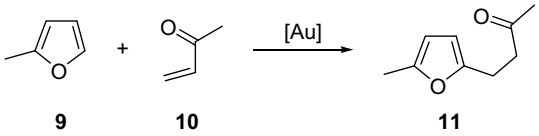
solvents but soluble in highly polar solvents such as CH_3CN. Spectroscopic and analytical data are consistent with the proposed structures.

The crystal structure of **8** has been determined by X-ray diffraction methods. A drawing of the cationic metallic part is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The Au^{III} center is located in a slightly distorted square-planar geometry, surrounded by two chlorine atoms and two nitrogen atoms. The Au–N bond lengths are 2.030(3) Å and 2.049(3) Å. These bond distances fall in the usual range found for this type of bonds in cationic [15–24] or even neutral complexes [25] [ranging from 2.018(10) to 2.055(11) Å]. The Au^{III}–Cl bond lengths are 2.2551(10) and 2.2636(10) Å, which are similar to those found in the literature [15–25]. Other internal bond parameters are as expected and do not deserve additional comments.

2.2. Catalytic studies of C–C and C–O bond formations

2.2.1. Addition of α,β-unsaturated ketones with furans and electron-rich arenes

Gold(III) compounds **5–8** have been evaluated in the addition of 2-methylfuran **9** to methyl vinyl ketone (MVK) **10** (Eq. (1))



(1)

Equation 1. Addition of MVK to 2-methyl furane catalyzed by the new gold(III) coordination complexes.

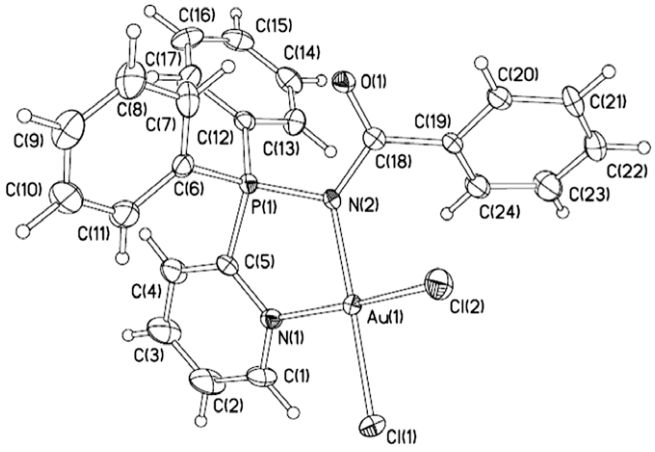


Fig. 1. Molecular drawing of the cation in $[Au(Ph_2PyP{=}NC(O)Ph)Cl_2]ClO_4$ **8**. Thermal ellipsoids are drawn at 50% probability.

Table 1
Selected bond lengths (Å) and angles (°) for **8**.

Au(1)–N(2)	2.030(3)	N(2)–Au(1)–N(1)	84.50(11)
Au(1)–N(1)	2.049(3)	N(2)–Au(1)–Cl(2)	93.41(8)
Au(1)–Cl(2)	2.2551(10)	N(1)–Au(1)–Cl(2)	172.85(8)
Au(1)–Cl(1)	2.2636(10)	N(2)–Au(1)–Cl(1)	177.83(8)
N(1)–C(1)	1.342(4)	N(1)–Au(1)–Cl(1)	93.35(8)
N(1)–C(5)	1.354(4)	Cl(2)–Au(1)–Cl(1)	88.77(4)
N(2)–C(18)	1.407(4)	C(1)–N(1)–C(5)	119.9(3)
N(2)–P(1)	1.656(3)	C(1)–N(1)–Au(1)	123.7(2)
P(1)–C(12)	1.784(3)	C(5)–N(1)–Au(1)	116.4(2)
P(1)–C(6)	1.790(4)	C(18)–N(2)–P(1)	115.6(2)
P(1)–C(5)	1.809(4)	C(18)–N(2)–Au(1)	129.5(2)

Reactions were run at RT and examined after 6 or 18 h (Table 2). The new gold coordination compounds are active in the absence of silver salts (entries 1, 5 and 9) and, moreover, the addition of silver salts does not increase the yields in a significant way. After the reaction time, decomposition of the catalyst is evident, since a gold mirror is formed. The comparison of complexes **5–8** as catalysts in this reaction with the previously reported neutral cycloaurated gold(III) compounds results in better conversions for the formers in absence of silver salts and similar yields in presence of silver salts. While **5–8** are air- and moisture-stable for months, even in solution, their stability after consumption of the reactants in this catalytic process is notably lower than that observed for the neutral cycloaurated gold(III) compounds and is similar to that found for $[AuCl_3\{N(=PPh_3)C(O)C_6H_4Me\text{-}2\}]$ [8]. Clearly the chelating effect of the two N donor atoms in the iminophosphorane complexes **5–8** confers a certain degree of stability to the Au(III) center.

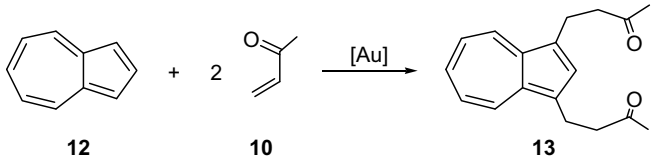
Table 2
Results of the addition reactions of methyl vinyl ketone (**10**) to 2-methylfuran (**9**).[a]

Entry	Catalyst (1 mol%)	Silver salt (mol%)	Time (h)	Yield (%)[b]
1	**5**	0	18	63
2	**5**	AgOTf (1.1)	18	59
3	**5**	AgOTf (2.2)	6	62
4	**5**	AgOTf (2.2)	18	75
5	**6**	0	18	76
6	**6**	AgOTf (1.1)	18	73
7	**6**	AgOTf (2.2)	6	75
8	**6**	AgOTf (2.2)	18	84
9	**8**	0	18	60
10	**8**	AgOTf (1.1)	18	71
11	**8**	AgOTf (2.2)	6	70
12	**8**	AgOTf (2.2)	18	79

[a] *Reaction conditions*: the reactions were performed at 25 °C in a kontex tube using 2 mmol of **9**, 2 mmol of **10**, 0.02 mmol of gold complex and 0.044 mmol (or 0.022 mmol) of silver salt in 5 mL of CH_3CN as solvent.

[b] Yields were obtained on isolated product. Details are given in Section 4.

On the other hand, the addition of acid-sensitive azulene **12** to MVK (**10**) with compounds **5**, **6** and **8** as catalysts (Eq. (2)) afforded high yields of **13** (90 ± 3% after 24 h). In this case the less acidic character of all the gold(III) organometallic and coordination complexes versus the acidic character of $AuCl_3$ may be responsible for a higher yield (with $AuCl_3$, 55% yield after 3 days) [13]



12 **10** **13** (2)

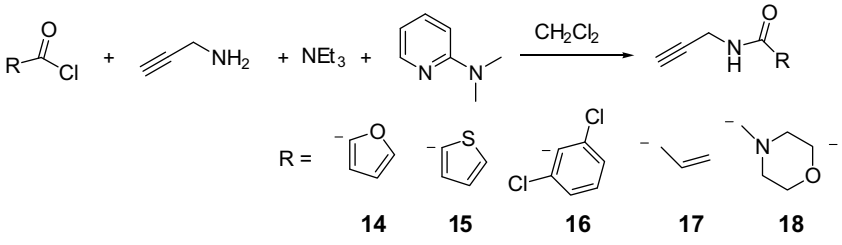
Equation 2. Addition of MVK **10** to azulene **12** catalyzed by the new gold(III) complexes. The reactions were performed at 25 °C in a kontex tube using 2 mmol of **10**, 2 mmol of **12**, 0.03 mmol of gold complex and 0.066 mmol of AgOTf in 5 mL of CH_3CN as solvent. Yields were obtained on isolated product. [Au] = **5**, **6** or **8**; time = 24 h; yield = 90±3%.

In order to detect some gold reaction intermediates we monitored the reaction of **9** with **10** in CD_3CN catalyzed by **8** by ^1H and ^{31}P NMR spectroscopy. The separate addition of **9** or **10** to CD_3CN solutions of **8** does not promote changes of the NMR parameters immediately or even after 30 min. When **9** is reacted with **10** in presence of stoichiometric amounts of **8** or substoichiometric (20%) amounts we did not observe changes in the NMR signals immediately after mixing, or after 30 min. After this period of time some changes are evident: the formation of **11** by consumption of **9** and **10** is clear, and it is accompanied by a high field shift of the ^{31}P signal (from 57.8 ppm to 24.9 and 24.2 ppm) and also by a high field shift of the peak due to the pyridinic ortho proton (from 9.70 ppm to about 9.00 ppm) for **8**. Similarly to what was observed in the catalytic process, once the reagents were consumed and **11** was formed, extensive decomposition to metallic gold was observed.

These observations are very similar to those reported for cycloaurated compounds, and also suggest that the limiting step of the catalytic cycle is the coordination of the substrates to the metallic center. Any other further steps should be very fast. To achieve the bonding of the incoming substrates, vacant coordination sites could be generated by, at least, two plausible ways: (i) dissociation of the iminophosphorane ligand; (ii) dissociation of a chloride ligand. Both processes are possible under the experimental reaction conditions. While we do not have evidence for halide dissociation, the iminophosphorane seems to leave the coordination sphere of the gold center during the catalytic cycle. This is suggested from the upfield shift of the P signal to a position intermediate between **8** (57.8 ppm) and the free ligand (14.8 ppm), probably indicating a fast equilibrium. Further addition of free ligand **4** to the mixture of **8**, **9** and **10** does not change the appearance of the spectrum (a single signal remains in the spectrum, although considerably broadened) but the observed average chemical shift moves to the high field region. This fact is in good agreement with an equilibrium involving the non bonded iminophosphorane. The same behaviour is observed for the signal due to the H_{ortho} of the pyridine fragment in the ^1H NMR spectrum, providing additional evidence. Therefore the chelate is not preserved during the catalytic cycle, at least in the NMR timescale. The data suggest that the iminophosphorane ligand behaves as an 'organic stabilizer' for a reactive form of gold. When the metal center is not involved in a catalytic cycle, the ligand confers a high stability to the complex, and **5–8** can be stored at air without precautions, but the 'organic wrapper' can be released easily if necessary (for instance, in a catalytic cycle).

2.2.2. Synthesis of 2,5-disubstituted oxazoles

Although substituted oxazole fragments are structural motifs that occur in a large number of natural products, a direct synthetic path in mild conditions to obtain oxazoles had not been described until 2004. Hashmi et al. reported that 2,5-disubstituted oxazoles could be synthesized from the corresponding propargylcarboxamides under mild reactions via homogeneous catalysis by $AuCl_3$ [13]. Later, two different groups (Hashmi et al. and Echavarren et al.) were able to identify a 5-methylene-4,5-dihydrooxazole [26] intermediate. The new air- and moisture-stable complexes **5–8** catalyze these reactions by activation of the alkyne moiety. The N-propargylcarboxamides (Eq. (3)) which have not been reported so far are characterized in Section 4

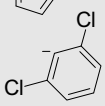
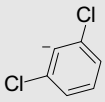
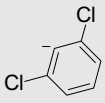
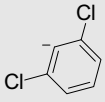
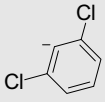
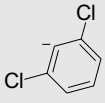


14 **15** **16** **17** **18** (3)

Equation 3. Synthesis of the different N-propargylcarboxamides (based on ref 13).

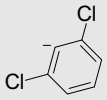
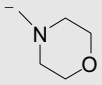
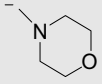
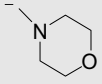
We found that **5–8** (5 mol%) were efficient catalysts in the cycloisomerization of propargylic amides in CH_2Cl_2, at RT and at air (Eq. (4)), and we did not observe decomposition after the reaction time. The results are collected in Table 3. The yields were

Table 3
Results of Au-catalyzed cycloisomerization of propargylic amides in CH_2Cl_2.

Entry	R	Catalyst (5 mol%)	Time (h)	Yield (%)[a]	Molar ratio final/intermediate[b]
1		$AuCl_3$	15	93	1/2.44
2		$AuCl_3$	48	95	1/0
3		**5**	72	90	1/0
4		**6**	15	100	¼
5		**6**	72	90	1/0
6		**7**	72	86	1/0
7		**8**	72	87	1/0
8		$AuCl_3$	15	95	1.26/1
9		$AuCl_3$	30	95	1/0
10		**5**	48	85	1/0
11		**6**	15	95	2/1
12		**6**	72	90	1/0
13		**7**	72	80	1/0
14		**8**	72	85	1/0
15		$AuCl_3$	15	97	2/1
16		$AuCl_3$	30	90	1/0
17		**5**	15	97	1/6.5
18		**5**	48	85	1/0
19		**6**	48	81	1/0
20		**7**	48	78	1/0

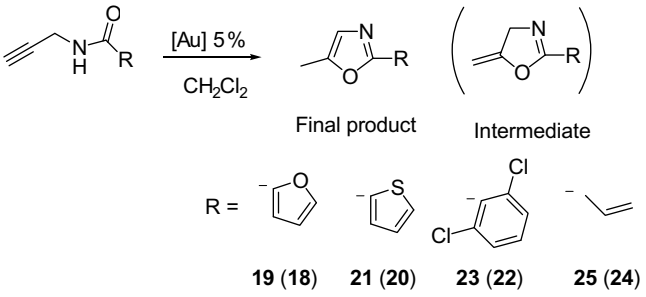
(*continued on next page*)

Table 3 (*continued*)

Entry	R	Catalyst (5 mol%)	Time (h)	Yield (%)[a]	Molar ratio final/intermediate[b]
21		**8**	48	80	1/0
22		$AuCl_3$	24	94	1/4.8
23		$AuCl_3$	48	94	1/4.8
24		**5**	48	80	0/1
25		$AuCl_3$	15	0	–
26		$AuCl_3$	30	0	–
27		**5**	30	0	–

[a] Isolated product.
[b] Determined by NMR.

equivalent to those described for $AuCl_3$ (R = furane; Table 3, entry 2) although reaction times were longer (usually in a ratio 2:3). In all the cases while monitoring the reaction by ^1H NMR we could observe the alkylidene-hydrooxazole intermediates (**19**, **20**, **22** and **24**)



Equation 4. Synthesis of the 2,5-Disubstituted oxazoles by Au -homogeneous catalysis (based on ref 13).

(4)

We tested the influence of different substituents in the cycloisomerization reaction. Reaction times were compared to those obtained by us with $AuCl_3$ (entries 1, 2, 8, 9, 15, 16, 22, 23, 25, 26). In most cases the behaviour of **5–8** was similar to that of $AuCl_3$ and they resulted effective catalysts, although longer reaction times were needed. In this manner 2-(2′-thienyl)-5-methylthiazole **21** can be prepared in good yields (entries 10–14). To the best of our knowledge **21** (with potential medicinal applications) had been prepared by a elimination reaction of a terminal β-oxy selenoxide in a two step procedure and with $H_2O_2/NaHCO_3$ as reagents [27]. This is a much improved method to obtain this oxazole. The oxazole **23** can be obtained in high yields with both $AuCl_3$ or **5–8**. This oxazole could be of interest due to the possibility of further functionalization using the halide groups, for instance, in Pd-catalysed CC coupling reactions (Stille, Heck, Suzuki, etc.). In the case of R = vinyl, final product **25** only could be obtained with $AuCl_3$ in a small yield (16%). Longer reaction times did not improve the results. With compound **5** we only got the intermediate product **24** and we did not find formation of the oxazole **25** after 48 h (entry 24). With R = morpholyl there was no conversion at all for either $AuCl_3$ or compound **5** (entries 25–27) showing the influence of electronic factors and intramolecular coordinating functionalities close to the reaction center [13]. These results are important since air-stable cationic coordination Au(III) complexes with chelating ligands have a catalytic efficiency in the reported processes comparable to that of $AuCl_3$. In addition, with catalysts **5–8** the reactions can be performed at air while reactions using $AuCl_3$ were run under a N_2 atmosphere.

The PR_3 fragment of the iminophosphorane motif has been used as a "spectroscopic marker" to follow reactions by ^{31}P NMR. We run a stoichiometric reaction of **8** and **16** (R = 2,4-$C_6H_3Cl_2$) in CD_2Cl_2 at RT and monitored by ^1H and ^{31}P NMR. Interestingly we found that the addition of the carboxamide **16** to a CD_2Cl_2 solution of **8** promotes the immediate disappearance of the ^{31}P peak at 56.8 ppm (pure **8**) and a singlet signal is seen instead at δ = 24.6 ppm. Further addition of free iminophosphorane **4** (14.8 ppm) gives an averaged broad signal shifted to high field. This fact suggests, as previously described for the additions of methyl-furan to MVK, the presence of a fast equilibrium. After de-coordination of the iminophosphorane ligand and/or a chloride ligand it seems sensible to assume the activation of the C–H bond of the C≡C–H motif from the N-propargylcarboxamide. Unfortunately, we were not able to identify gold-alkyne or gold-vinylidene intermediates [13].

3. Conclusion

We have prepared new air- and moisture-stable gold(III) complexes with N,N-chelating iminophosphorane ligands that are efficient catalysts in the addition of 2-methylfuran and azulene to MVK in the presence of silver salts. These derivatives behave as efficient catalysts in the preparation of oxazoles by cycloisomerization reactions of N-propargylcarboxamides at air. The gold catalytically active species are formed by partial dissociation of the iminophosphorane ligand and by dissociation of at least one chloride ligand. Subsequent coordination of organic substrates is fast and we have not observed these gold intermediates by NMR.

4. Experimental

General procedures are as reported elsewhere [8]. Iminophosphoranes **1–3** [28–30] and N-propargylcarboxamides **14** [13], **17** [31], and **18** [32] were prepared as previously described. *Caution:* perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and all samples handled with great caution. Organic azides are *highly hazardous* materials which can explode, and whose preparation and manipulation must be carried out with maximum caution. They must be stored at low *T* (≈*0* °C) and dissolved in an inert solvent.

4.1. Syntheses

4.1.1. Syntheses of the iminophosphorane ligand [Ph_2PyP=N-C(O)-Ph] (**4**)

To a solution of benzoyl azide (0.615 g, 4.18 mmol) in CH_2Cl_2 (20 mL) a solution of PPh_2Py (1.100 g, 4.18 mmol) in 20 mL of CH_2Cl_2 was added dropwise. The reaction mixture was stirred at RT until evolution of N_2 gas was completed. The resulting yellow solution was concentrated ca. 1–2 mL and by addition of 15 mL of Et_2O a white solid precipitated in the reaction media. The crude (**4**) was filtered, washed with 10 mL of Et_2O and vacuum dried. Yield: 1.806 g, 2.84 mmol, 67.9%. Anal. Calc. for $[C_{24}H_{19}N_2OP]$ (382.39): C, 75.38; H, 5.01; N, 7.32. Found: C, 75.21; H, 5.21; N, 7.37%. MS (FAB+): 383 (85%) $[M+H]^+$. IR: υ(C=O) = 1592 cm^{-1}; υ(N=P) = 1349 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 14.80. ^1H NMR ($CDCl_3$): δ = 7.32–7.39 (m, 8H, H_m, $PPh_2 + H_m + H_p$, PhCO + H_4, C_6H_4N), 7.44–7.47 (m, 2H, H_p, PPh_2), 7.75 (tdd, 1H, H_5, C_6H_4N, $^4J_{HP}$ = 7.7, $^3J_{HH}$ = 4.2, $^4J_{HH}$ = 1.4), 7.85–7.90 (m, 4H, H_o, PPh_2), 8.29–8.33 (m, 3H, H_6, $C_6H_4N + H_o$, PhCO), 8.69 (d, 1H, H_3, C_6H_4N, $^3J_{HH}$ = 4.5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 125.48 (d, C_4, C_6H_4N, $^4J_{PC}$ = 3.2), 127.34 (s, C_m, PhCO), 127.74 (d, C_i, PPh_2, $^1J_{PC}$ = 100.0), 128.43 (d, C_m, PPh_2, $^3J_{PC}$ = 12.4), 129.58 (d, C_o, PhCO,$^4J_{PC}$ = 2.4), 129.75 (d, C_6, C_6H_4N, $^2J_{PC}$ = 20.8), 130.86 (s, C_p, PhCO), 132.21 (d, C_p, PPh_2, $^4J_{PC}$ = 2.9), 133.50 (d, C_o, PPh_2, $^2J_{PC}$ = 9.6), 136.71 (d, C_5, C_6H_4N, $^3J_{PC}$ = 9.3), 138.35 (d, C_1, PhCO, $^3J_{PC}$ = 19.7), 150.36 (d, C_3, C_6H_4N, $^3J_{PC}$ = 19.4), 152.95 (d, C_1, C_6H_4N, $^1J_{PC}$ = 129.0), 176.78 (d, CO, $^2J_{PC}$ = 8.0).

4.1.2. Syntheses of gold(III) compounds $[AuCl_2(N,N\text{-}IM)]ClO_4$ (**5–8**)

*4.1.2.1. Synthesis of $[Au(Ph_3P{=}NR)Cl_2]ClO_4$: R = CH_2-2-NC_5H_4 (**5**), CO-2-NC_5H_4 (**6**).* To a solution of $K[AuCl_4]$ (0.205 g; 0.54 mmol) in CH_3CN (20 ml), $AgClO_4$ (0.247 g, 1.19 mmol) was added. The resulting yellow reaction mixture was stirred at room temperature during 30 min and subsequently filtered through a celite pad (to remove the AgCl formed). To the resulting yellow solution **1** (0.200 g, 0.54 mmol) was added. $KClO_4$ precipitated immediately in the reaction media and after 1 h stirring at RT the reaction mixture was filtered through a celite pad. The resulting yellow solution was concentrated under vacuum to ca. 1–2 mL. By addition of 15 mL of Et_2O **5** is obtained as a yellow solid that was filtered, washed with 10 mL of Et_2O and dried under vacuum. Yield: 0.283 g, 0.38 mmol, 70.9%. Complex **5** was recrystallized from CH_2Cl_2/Et_2O, affording crystals of **5** · CH_2Cl_2, which were used for analytic and spectroscopic measurements. Anal. Calc. for $[C_{24}H_{21}AuCl_3N_2O_4P]CH_2Cl_2$ (735.75): C, 36.58; H, 2.82; N, 3.41. Found: C, 36.33; H, 2.71; N, 3.64%. MS (FAB+): 636 (75%) $[M-ClO_4]^+$. IR: υ (*N=P*) = 1275 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 43.54. ^1H NMR ($CDCl_3$): δ = 4.92 (d, 2H, CH_2, $^4J_{HH}$ = 4.3), 7.67–7.72 (m, 7H, H_4, $C_6H_4N + H_m$, PPh_3), 7.79–7.91 (m, 10H, H_6, $C_6H_4N + H_o + H_p$, PPh_3), 8.19 (td, 1H, H_5, C_6H_4N, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 0.9), 9.26 (d, 1H, H_3, C_6H_4N, $^3J_{HH}$ = 7.3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 61.06 (d, CH_2, $^2J_{PC}$ = 4.0), 122.29 (d, C_i, PPh_3, $^1J_{PC}$ = 102.6), 124.16 (s, C_4, C_6H_4N), 125.69 (s, C_6, C_6H_4N), 129.94 (d, C_m, PPh_3, $^3J_{PC}$ = 13.2), 134.04 (d, C_o, PPh_3, $^2J_{PC}$ = 10.5), 134.92 (d, C_p, PPh_3, $^4J_{PC}$ = 3.0), 143.73 (s, C_5, C_6H_4N), 146.12 (s, C_3, C_6H_4N). Signals due to C_1 (NC_5H_4) were not observed.

Compound **6** was obtained in the same way starting from 0.198 g (0.52 mmol) of $K[AuCl_4]$, $AgClO_4$ (0.239 g, 1.15 mmol) and ligand **2** (0.200 g, 0.52 mmol). Yield: 0.283 g, 0.38 mmol, 70.9%. Anal. Calc. for $[C_{24}H_{19}AuCl_3N_2O_5P]$ (749.41): C, 38.46; H, 2.55; N, 3.74. Found: C, 38.21; H, 2.56; N, 3.70%. MS (FAB+): 650 (80%) $[M-ClO_4]^+$. IR: υ(C=O) = 1698 cm^{-1}, υ(N=P) = 1263 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 39.00. ^1H NMR ($CDCl_3$): δ = 7.64–7.77 (m, 9H, H_m, $PPh_3 + H_p$, PPh_3), 8.00–8.15 (m, 8H, $H_4 + H_6$, $C_6H_4N + H_o$, PPh_3), 8.37 (td, 1H, H_5, C_6H_4N, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.1), 9.50 (dd, 1H, H_3, C_6H_4N, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.0). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 121.06 (d, C_i, PPh_3, $^1J_{PC}$ = 109.8), 128.58 (s, C_4, C_6H_4N), 131.15 (s, C_6, C_6H_4N), 129.73 (d, C_m, PPh_3, $^3J_{PC}$ = 13.7), 134.09 (d, C_o, PPh_3, $^3J_{PC}$ = 11.4), 134.78 (d, C_p, PPh_3, $^4J_{PC}$ = 2.9), 137.25 (s, C_5, C_6H_4N), 144.53 (s, C_3, C_6H_4N), 176.99 (s, CO). Signals due to C_1 (NC_5H_4) were not observed, even when long accumulation times were used.

*4.1.2.2. Synthesis of $[AuCl_2(Ph_2PyP{=}NR)]ClO_4$: R = Ph (**7**), C(O)-Ph (**8**).* Compound **7** was obtained in the same way starting from 0.192 g (0.51 mmol) of $K[AuCl_4]$, $AgClO_4$ (0.232 g, 1.2 mmol) and ligand **3** (0.180 g, 0.51 mmol). Yield: 0.258 g, 0.36 mmol, 70.4%. Anal. Calc. for $[C_{23}H_{19}AuCl_3N_2O_4P]$ (721.69): C, 38.24; H, 2.65; N, 3.88. Found: C, 38.30; H, 2.75; N, 3.86%. MS (FAB+): 622 (20%) $[M-ClO_4]^+$. IR: υ(N=P) = 1299 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 59.41. ^1H NMR ($CDCl_3$): δ = 6.99–7.04 (m, 3H, $H_o + H_p$, Ph), 7.17 (t, 2H, H_m, Ph, $^3J_{HH}$ = 7.2), 7.62–7.71 (m, 5H, H_6, $C_6H_4N + H_m$, PPh_2), 7.77–7.82 (m, 2H, H_p, PPh_2), 7.93–8.06 (m, 5H, H_4, $C_6H_4N + H_o$, PPh_3), 8.22 (t, 1H, H_5, C_6H_4N, $^3J_{HH}$ = 6.7), 9.10 (d, 1H, H_3, C_6H_4N, $^3J_{HH}$ = 6.4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 118.93 (d, C_i, PPh_2, $^1J_{PC}$ = 102.3), 120.30 (d, C_o, Ph, $^3J_{PC}$ = 6.9), 124.15 (s, C_p, Ph), 128.19 (d, C_4, C_6H_4N, $^4J_{PC}$ = 3.7), 129.67 (s, C_m, Ph), 130.16 (d, C_m, PPh_2, $^3J_{PC}$ = 13.6), 131.04 (d, C_5, C_6H_4N, $^3J_{PC}$ = 23.0), 134.04 (d, C_o, PPh_2, $^2J_{PC}$ = 11.0), 135.56 (d, C_p, PPh_2, $^4J_{PC}$ = 3.1), 137.50 (d, C_1, Ph, $^2J_{PC}$ = 5.0), 138.22 (d, C_6, C_6H_4N, $^2J_{PC}$ = 10.7), 145.92 (d, C_1, C_6H_4N, $^1J_{PC}$ = 130.1), 151.83 (d, C_3, C_6H_4N, $^3J_{PC}$ = 21.2).

Compound **8** was obtained in the same way starting from 0.239 g (0.52 mmol) of $K[AuCl_4]$, $AgClO_4$ (0.239 g, 1.15 mmol) and ligand **4** (0.200 g, 0.52 mmol). Yield: 0.245 g, 0.33 mmol, 62.5%. Anal. Calc. for $[C_{24}H_{19}AuCl_3N_2PO_5]$ (749.41): C, 38.46; H, 2.55; N, 3.74. Found: C, 39.22; H, 3.18; N, 3.39%. MS (FAB+): 650 (25%) $[M-ClO_4]^+$. IR: υ(C=O) = 1637 cm^{-1}; υ(N=P) = 1290 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_3CN): δ = 56.20. ^1H NMR (CD_3CN): δ = 7.53 (t, 2H, H_m, PhCO, $^3J_{HH}$ = 8.0), 7.69 (t, 1H, H_p, PhCO, $^3J_{HH}$ = 8.0), 7.74–7.80 (m, 4H, H_m, PPh_2), 7.93–8.05 (m, 6H, $H_o + H_p$, PPh_2), 8.15 (d, 2H, H_o, PhCO, $^3J_{HH}$ = 8.0), 8.20–8.29 (m, 2H, $H_4 + H_6$, C_6H_4N), 8.55 (tdd, 1H, H_5, C_6H_4N, $^3J_{HH}$ = 6.7, $^4J_{HP}$ = 3.8, $^4J_{HH}$ = 1.3), 9.67 (d, 1H, H_3, C_6H_4N, $^3J_{HH}$ = 5.9). $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 118.35 (d, C_i, PPh_2, $^1J_{PC}$ = 101.5), 128.71 (s, C_m, PhCO), 130.01

(s, C_o, PhCO), 130.45 (d, C_m, PPh_2, $^3J_{PC}$ = 14.5), 132.39 (d, C_4, C_6H_4N, $^4J_{PC}$ = 2.2), 134.04 (C_6, C_6H_4N, overlapped with C_i, PhCO), 134.09 (s, C_p, PhCO), 134.37 (d, C_o, PPh_2, $^2J_{PC}$ = 12.9), 136.89 (d, C_p, PPh_2, $^4J_{PC}$ = 3.1), 145.30 (d, C_5, C_6H_4N, $^3J_{PC}$ = 9.8), 148.94 (d, C_1, C_6H_4N, $^1J_{PC}$ = 123.0), 151.75 (d, C_3, C_6H_4N, $^3J_{PC}$ = 7.7), 174.83 (s, CO).

4.1.3. Syntheses of N-propargylcarboxamides **15** and **16**

To a solution of propargylamine (1 mL, 14.5 mmol), NEt_3 (2 mL, 14.5 mmol) and N,N-dimethylpyridine (0.035 g, 0.25 mmol) in 40 mL of CH_2Cl_2 at 0 °C a solution of 2-thiophenoyl chloride (1.5 mL, 14.5 mmol) in 5 mL of CH_2Cl_2 was added dropwise. The resulting yellow solution was stirred at 0 °C during 30 min and a further 3 h at room temperature. The reaction mixture was then washed with a saturated solution of NH_4Cl (2 × 20 mL) and a saturated solution of $NaHCO_3$ (2 × 20 mL). The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated to ca. 1–2 mL. The addition of 15 mL of Et_2O afforded a white solid (**15**) that was subsequently filtered, washed with 15 mL of Et_2O and vacuum dried. Yield: 1.425 g, 8.62 mmol, 59.4%. Anal. Calc. for [C_8H_7NOS] (165.21): C, 58.16; H, 4.27; N, 8.47; S, 19.4. Found: C, 58.30; H, 4.39; N, 8.57; S, 19.5%. MS (ESI$^+$): 188 (100%) [M+Na]$^+$. ^{1}H NMR ($CDCl_3$): δ = 2.22 (t, 1H, HC≡C, $^4J_{HH}$ = 2.5), 4.17 (dd, 2H, CH_2, $^3J_{HH}$ = 5.3, $^4J_{HH}$ = 2.5), 6.32 (br. s, 1H, NH), 7.01 (dd, H_4, C_4H_3S, $^3J_{H4-H3}$ = 3.7, $^4J_{H4-H5}$ = 5.0), 7.43 (dd, H_5, C_4H_3S, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 1.1), 7.50 (dd, H_3, C_4H_3S, $^3J_{HH}$ = 3.7, $^4J_{HH}$ = 1.1). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 29.66 (s, CH_2), 71.81 (s, C≡C), 79.44 (s, HC≡C), 127.75 (s, C_4, C_4H_3S), 128.69 (s, C_3, C_4H_3S), 130.49 (s, C_5, C_4H_3S), 138.16 (s, C_1, C_4H_3S), 161.82 (s, CO).

Compound 1**6** was obtained in the same way starting from propargylamine (1 mL, 14.5 mmol); NEt_3 (2 mL, 14.5 mmol) and N,N-dimethylpyridine (0.035 g, 0.25 mmol) in 40 mL of CH_2Cl_2 and a solution of 2,6-dichlorobenzoylchloride (2.1 mL, 14.5 mmol) in 5 mL of CH_2Cl_2 at 0 °C. Yield: 1.993 g, 8.74 mmol, 60.3%. Anal. Calc. for [$C_{10}H_7NOCl_2$] (228.07): C, 52.66; H, 3.09; N, 6.14. Found: C, 52.64; H, 3.15; N, 6.16%. MS (ESI$^+$): 250 (100%) [M+Na]$^+$. ^{1}H NMR ($CDCl_3$): δ = 2.30 (t, 1H, HC≡C, $^4J_{HH}$ = 2.5), 4.28 (dd, 2H, CH_2, $^3J_{HH}$ = 5.3, $^4J_{HH}$ = 2.5), 6.02 (br. s, 1H, NH), 7.24–7.34 (m, 3H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 29.62 (s, CH_2), 73.10 (s, C≡C), 78.54 (s, HC≡C), 128.00 (s, C_p, Ph), 130.82 (s, C_m, Ph), 132.29 (s, C_o, Ph), 135.20 (s, C_1, Ph), 164.28 (s, CO).

4.2. Catalytic studies

4.2.1. Addition of methyl vinyl ketone **10** with 2-methylfuran (**9**) or azulene (**12**)

All catalytic reactions were performed at 25 °C in a Kontex tube using distilled and degassed solvents and under Argon atmosphere. Procedure for the addition of MVK (**10**) to 2-methylfuran (**9**): 2 mmol of **10**, 2 mmol of **9**, 0.02 mmol of the corresponding gold complex and 0.044 mmol (or 0.022 mmol) of silver salt (when necessary) were mixed in 5 mL of CH_3CN, and this mixture was stirred for a period of 6 or 18 h (Table 1). After the reaction time was completed, the resulting mixture was filtered through a short silica-gel column using 20 mL of a Et_2O/*n*-hexane (3/1) mixture as eluent. The yellow solution was evaporated to dryness under vacuum, affording pure **11**. Procedure for the addition of MVK (**9**) to azulene (**12**): 2 mmol of **12**, 2 mmol of **9**, 0.03 mmol of the corresponding gold complex (0.02 mmol in the case of $AuCl_3$) and 0.066 mmol of silver salt (when necessary) were mixed in 5 mL of CH_3CN, and this mixture was stirred for 24 h (Table 2). After the reaction time, the resulting mixture was filtered through a short silica-gel column using 20 mL of a Et_2O/*n*-hexane (3/1) mixture as eluent. The yellow solution was evaporated to dryness under vacuum, affording pure **13**.

4.2.2. Synthesis of 2,5-disubstituted oxazoles and of compound **29**

To solutions of 0.63 mmol of N-propargylcarboxamides **14–18** and **27** in dry CH_2Cl_2, 5 mol% of gold compound (either $AuCl_3$ or **5–8**) was added. In the case of **5–8** the reactions can be performed at air. The reaction mixture was stirred at the temperature and during the time specified in Table 3. The reaction mixture was filtered through a celite pad to remove any gold source and the resulting solutions were evaporated to dryness. Conversions shown in Table 3 (and molar ratios intermediate/final product) were obtained by ^{1}H NMR analysis of the isolated products.

4.3. Crystal structure determination of **8**

Single crystals of **8** were grown by diffusing Et_2O into a NCMe solution of complex [$AuCl_2(Ph_2PyP{=}NC(O)Ph)]ClO_4$ (**8**). A yellow prism of dimensions 0.16 × 0.11 × 0.07 mm^3 was mounted at the end of a quartz fiber in a random orientation, covered with magic oil and placed under a cold stream of nitrogen. Data collection was performed at 150 K on a Oxford Diffraction Xcalibur2 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An hemisphere of data was collected based on three ω-scan and φ-scan runs. The diffraction frames were integrated using CRYSALIS RED [33] and the integrated intensities were corrected for absorption with SADABS [34].

4.3.1. Crystal data and data collection parameters

Compound **8**: $C_{24}H_{19}AuCl_3N_2O_5P$, M = 749.90, Triclinic, space group $P\bar{1}$, a = 8.5748(6) Å, b = 9.426(3) Å, c = 16.233(4) Å, α = 88.13(2)°, β = 82.241(11)°, γ = 79.843(12)°, V = 1279.6(5) Å^3, T = 150(2) K, Z = 2, D_{cal} = 1.946 mg m^{-3}, F(000) = 724, μ = 6.164 mm^{-1}, θ range 2.52–25.00°, 22 771 reflections collected, 4498 independent (R_{int} = 0.0377).

4.3.2. Structure solution and refinement

The structure was solved and developed by direct methods [35]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in idealized positions and treated as riding atoms. Each H atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the parent atom. The structure was refined to F_o^2, and all reflections were used in the least-squares calculations [36]. Refinement proceeded to: R = 0.0197, wR = 0.0415 for 362 parameters, and R = 0.0256, wR = 0.0421 for all data, residual electron density in the range 1.002 and −0.533 e Å^{-3}.

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Appendix A. Supplementary material

CCDC 684707 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.058.

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