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Organometallic gold(III) and gold(I) complexes as catalysts for the 1,3-dipolar cycloaddition to nitrones: synthesis of novel gold–nitrone derivatives

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Abstract

Gold(III) and gold(I) anionic salts mediate the 1,3-dipolar cycloaddition of N-benzyl-C(2-pyridyl)nitrone (2-PyBN) (**1**) and methyl acrylate (**2**) (gold 5–10 mol% with respect to the nitrone) decreasing the reaction time and favouring the formation of the *exo* (*cis*) isomer. The best catalyst found was $Na[AuCl_4]$ (**7**) able to perform the addition reaction in 56 h (instead of the 96 h required for the control experiment) and giving an *endo*/*exo* relation between isomers of 44/56 (as opposed to 73/27, blank reaction). The catalytic activity of several organometallic gold complexes with the radicals pentafluorophenyl (C_6F_5) or mesityl ($2,4,6\text{-}(CH_3)_3C_6H_2$) has been also investigated. In some cases the activity is very similar to that obtained with inorganic salts. With the aim of identifying possible metallic intermediates in the cycloaddition reaction, novel gold(III) and gold(I) nitrone derivatives such as $[Au(C_6F_5)Cl_2(2\text{-PyBN})]$ (**21**), $[Au(C_6F_5)_2Cl(2\text{-PyBN})]$ (**22**) and $[Au(C_6F_5)(2\text{-PyBN})]$ (**23**) have been prepared and characterized. The reaction between $[AuCl_3(tht)]$ and 2-PyBN unexpectedly affords the ionic compound [2-PyBN–H][$AuCl_4$] (**5**) which also displays catalytic activity and moderate regioselectivity and whose crystal structure has been confirmed by X-ray studies.

Keywords: Dipolar cycloadditions; Nitrones; Gold; Organometallic; Crystal structure

1. Introduction

The use of Lewis-acid catalysts in modern organic synthesis has been expanding uninterruptedly during the last decade [1]. Nowadays the research is targeting more versatile, more selective, and more reactive catalysts. Carbon–carbon bond formation is one of the most important organic processes that can be Lewis-acid promoted. It has been found recently that *anhydrous* $AuCl_3$ catalyzes the formation of C–C and C–O bonds behaving as an effective Lewis-acid catalytic system [2]. Some examples include Michael type additions, selective cross cycloisomerization/dimerization of propargyl or allenyl ketones, benzannulation between *o*-alkynylbenzaldehydes and alkynes or cyclization of alkenyl furans. It is noteworthy that some of these reactions [2a] can be also catalyzed by silver salts but with much lower yields. Our research group has recently studied the 1,3-dipolar cycloaddition between nitrones and alkenes mediated by Lewis acids [3,4]. Despite the extensive study performed in this field by several laboratories [5] there are not that many examples in which a metallic complex with a nitrone as ligand catalyzes the dipolar cycloaddition. Most of these reactions require the presence of a metallic complex and the nitrone in a 1:1 molar ratio. We have shown, in previous reports, that stoichiometric reactions of the N-benzyl-C(2-pyridyl)nitrone with different dipolarophiles in the presence of zinc and silver compounds afforded an increase of both the reaction rate and the selectivity, favouring the formation of one of the possible isomers. The existence of zinc and silver-nitrone

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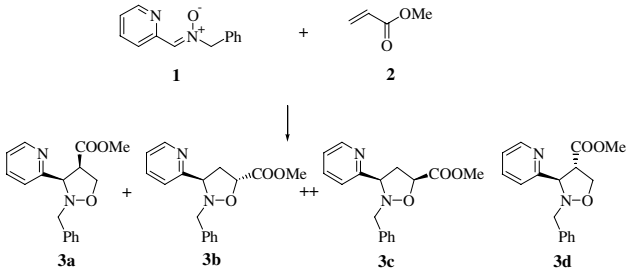
complexes during the reaction, which behave as intermediates in the cycloaddition process, was confirmed by different structural techniques [3,4].

We have also recently reported on the Lewis acidic behaviour exhibited by organometallic gold(III) complexes in the addition of nucleophiles to triple bonds [6]. In view of the results obtained with silver derivatives in the 1,3-dipolar cycloaddition of nitrones to alkenes [5] and in order to test the potential Lewis acidic character of gold(III) and gold(I) complexes, we decided to study their behaviour in cycloaddition reactions. Interestingly, we have found that they can be used not only as stoichiometric reagents but they can also mediate these cycloadditions in catalytic amounts (5–10 mol% with respect to the nitrone). Here we present the results on the 1,3-dipolar cycloaddition reaction of the N-benzyl-C(2-pyridyl)nitrone (2-PyBN), **1**, and methyl acrylate, **2**, (Eq. (1)) catalyzed by gold(III) and gold(I) derivatives. Novel gold(III) and gold(I)-nitrone derivatives will be described.

2. Results and discussion

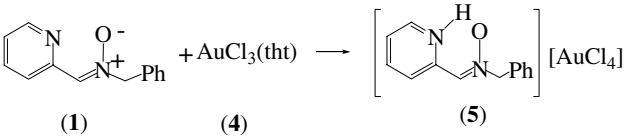
In the absence of catalyst, the reaction shown in Eq. (1) takes place in refluxing acetone after four days giving the two 3,5-disubstituted regioisomers (*endo* **3b** and *exo* **3c**) as major products (73% and 17%, respectively). Of the two possible 3,4 regioisomers (*endo* **3d** and *exo* **3a**) only the *exo* isomer **3a** could be detected in the reaction mixture (ca. 10%).



(1)

We studied the effect of the addition of gold(III) salts in catalytic amounts (5 or 10 mol%) to the cycloaddition reaction. Thus, we started our study with the coordination compound $[AuCl_3(tht)]$ (**4**) that is quite similar to *anhydrous* $AuCl_3$ but much more stable in solid state and solution, and easier to prepare and handle. Compound **4** has got labile tetrahydrothiophene (tht) as one of the ligands. The addition of 10 mol% of $[AuCl_3(tht)]$ to the reaction mixture reduces the reaction time from 4 to 3 days modifying the regioselectivity of the process affording an *endo*/*exo* mixture of isomers in a 55/45 ratio, respectively (Table 1, entries 1 and 2).

In order to explain the catalytic activity of **4** we carried out stoichiometric reactions between compound **4** and nitrone **1** and between this compound and the dipolarophile **2**. However, we only could observe reaction in the first case (Eq. (2)). Nevertheless, instead of the expected $[AuCl_3(2\text{-PyBN})]$ gold(III) complex, due to the plausible displacement of labile tht and a subsequent coordination of the nitrone **1** to the metallic centre, the ionic complex $[2\text{-PyBN–H}][AuCl_4]$ (**5**) was obtained. Complex **5** is always the product of the reaction independently on the reaction conditions used (different solvents, including dried toluene, dichloromethane, or tetrahydrofurane, and working under argon atmosphere).



(2)

The ^1H NMR spectrum at room temperature of complex **5** displays the corresponding N–H signal at 16.5 ppm as a broad singlet as well as signals downfield displaced from the usual nitrone resonances, except the signal due to the proton belonging to the carbon in α position, which is displaced from 8.60 ppm in the free nitrone to 8.42 ppm in **5**.

The ionic nature of complex **5** and the presence of such N–H bond was further elucidated by X-ray diffraction studies. A drawing of the molecule (anion and

Table 1
Catalytic activity of gold(III) and gold(I) salts and complexes in the 1,3-cycloaddition reaction of **1** and **2**

Entry	Compound	Catalyst (mol%)	Isomers (%) *endo*/*exo*	Time (h)	Conversion (%)[a]
1	None	–	73/27	96	100
2	$[AuCl_3(tht)]$ (**4**)	10	55/45	72	100
3	$[2\text{-PyBN–H}][AuCl_4]$ (**5**)	5	54/46	62	100
4	[2-PyBN–H]Tfo (**6**)	5	63/37	72	100
5	$Na[AuCl_4]$ (**7**)	5	44/56	54	100
6	$PPN[AuCl_4]$ (**8**)	5	59/41	56	100
7	$PPN[AuCl_4]$ (**8**)	10	57/43	46	100
8	$PPN[AuCl_2]$ (**9**)	10	54/46	56	100
9	[AuCl(tht)] (**10**)	10	56/44	76	100

[a] Conversion and selectivity measured by ^1H NMR ($CDCl_3$).

cation) is shown in Fig. 1, while selected bond and angles are presented in Table 2. In this case, and as previously shown for the nitrone 2-PyBN, **1** [3], the system C–CH=$N^+(O^-)$C of the nitrone and the heterocyclic ring are in the same plane. However, and as opposed to the free nitrone, the pyridinic nitrogen is *syn* periplanar to the oxygen of the nitrone group. This could be due to an interaction between the oxygen atom of the nitrone group and the hydrogen that belongs to the N–H bond. The distance found between the O and the H is 1.95(4) Å, which is 0.65 Å shorter than the sum of the van der Waals radii ($r_{vdW}(H) = 1.20$ Å and $r_{vdW}(O) = 1.40$ Å) [7]. Bond lengths and angles in the nitrone molecule are similar to those found in the free nitrone. Thus, the distances in the N–O and N–C units in **5** are 1.293(3) and 1.298(5) Å, respectively and 1.300(3) and 1.299(3) Å in **1**. Anion $[AuCl_4]^-$ displays a square-planar rearrangement for the metallic centre. Similar Au–Cl distances and angles have been found recently in oxonium ion compounds of different crown ethers with tetrachloroaurate as the counterion [8].

The protonation of the nitrone can be achieved directly by equimolecular reaction of **1** with triflic acid (Eq. (3)) affording [2-PyBN–H]Tfo, **6**, which shows almost identical spectroscopic data to those obtained for **5**.

2-PyBN + HTfo ⟶ [2-PyBN–H]Tfo (**6**) (3)

We carried out the same catalytic experiment (described in Eq. (1)) with [2-PyBN–H][$AuCl_4$] (**5**) and [2-PyBN–H]Tfo (**6**) as catalysts, in order to establish if the catalytic activity was due to the protonation of the nitrone or to the effect of the $[AuCl_4]^-$ anion (Table 1, entries 3 and 4). The obtained results led us to consider that the gold(III) anion was partly responsible for the catalytic activity and the moderated regioselectivity observed. This fact was subsequently confirmed by the catalytic activity and regioselectivity exhibited by other gold(III) anionic salts (entries 5–7) such as Na[$AuCl_4$], **7** or the less hygroscopic salt with the bulkier cation PPN^+ (bis(triphenylphosphine)iminium), PPN[$AuCl_4$], **8**.

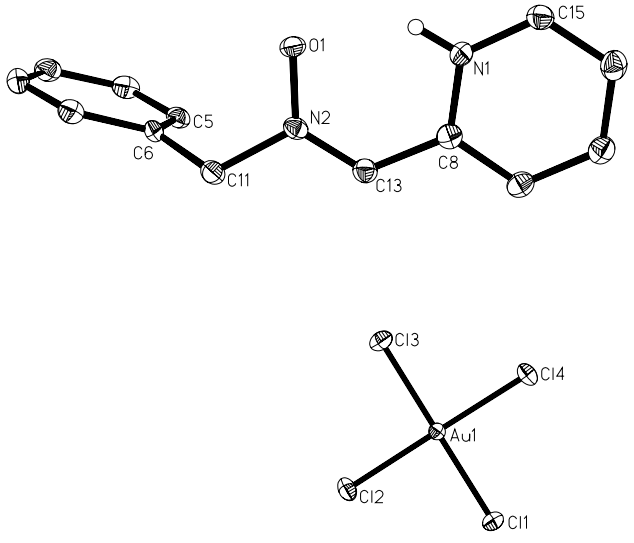


Fig. 1. View of the molecular structure of **5** (ellipsoids are drawn at 50% probability level). H atoms have been omitted for clarity.

Table 2
Bond lengths (Å) and angles (°) for [2-PyBN–H][$AuCl_4$] (**5**)

Bond lengths	
Au(1)–Cl(1)	2.2696(8)
Au(1)–Cl(4)	2.2756(8)
Au(1)–Cl(3)	2.2776(8)
Au(1)–Cl(2)	2.2870(8)
C(15)–N(1)	1.329(4)
N(1)–C(8)	1.353(4)
N(2)–O(1)	1.293(3)
N(2)–C(13)	1.298(5)
N(2)–C(11)	1.481(4)
C(8)–C(13)	1.440(5)
Bond angles	
Cl(1)–Au(1)–Cl(4)	90.59(3)
Cl(1)–Au(1)–Cl(3)	179.41(3)
Cl(4)–Au(1)–Cl(3)	89.18(3)
Cl(1)–Au(1)–Cl(2)	89.08(3)
Cl(4)–Au(1)–Cl(2)	178.96(2)
Cl(3)–Au(1)–Cl(2)	91.16(3)
N(1)–C(15)–C(16)	120.2(3)
C(2)–C(3)–C(4)	119.9(3)
C(15)–N(1)–C(8)	122.9(3)
O(1)–N(2)–C(13)	124.4(3)
O(1)–N(2)–C(11)	115.2(2)

The addition of 5 mol% of **7** produces a great change in the regioselectivity (from a ratio *endo*/*exo* of 73/27 in the absence of catalyst (entry 1) to an *endo*/*exo* ratio of 44/56 (entry 5)). Besides, the addition of gold salts decreases the reaction time in all cases and, specifically, the addition of 10 mol% of **8** decreases this time to less than half the value (entry 7) for the control experiment (entry 1).

To the best of our knowledge the addition of gold(I) derivatives in C–C and C–O coupling reactions have shown to be ineffective [2]. Nevertheless, we decided to study if gold(I) salts could display catalytic activity in the cycloaddition reaction object of our investigations. Unexpectedly, the addition of 10 mol% of PPN[$AuCl_2$], **9** or [AuCl(tht)], **10** to the reaction (Eq. (1)) reduces considerably the reaction time (from 96 to 56 h in the first case) and, reasonably in the second case (Table 1, entries 8 and 9, respectively). In addition, the regioselectivity is similar to that found in the addition of the gold(III) derivatives.

Recently, our research group has shown that anionic or neutral organometallic gold(III) complexes where one or more chlorides have been replaced by an organic group, like C_6F_5 or 2,4,6-$(CH_3)_3C_6H_2$ (mes), behave in a similar way to Na[$AuCl_4$], being efficient catalysts for

the addition of water and alcohols to terminal alkynes [6]. These complexes have the general formula Q[AuRCl$_3$] (Q = BzPPh$_3$, PPN; R = mes, C_6F_5), [Au(C_6F_5)Cl$_2$]$_2$, *trans*-NBu$_4$[Au(C_6F_5)X$_2$], X = Cl, Br and [Au(C_6F_5)$_2$Cl]$_2$. The organic groups attached to the gold(III) centres, pentafluorophenyl (C_6F_5) and mesityl (2,4,6-(CH$_3$)$_3$C$_6$H$_2$) were chosen because they are very different in their esteric and electronic properties. We considered that the evaluation of organometallic gold(III) compounds in several catalytic reactions could be of help in order to identify possible intermediates in some of these reactions. The organic groups could help not only to stabilize the plausible gold(III) complexes generated but also, they can be of aid in the identification of these metallic intermediates by "labelling" the gold(III) centres for structural techniques such as NMR spectroscopy.

The catalytic results for several organometallic gold(III) compounds (numbered in the tables and throughout the text) tested in the 1,3-cycloaddition reaction of **1** to **2** (Eq. (1)) are collected in Table 3. There is always an increase of the reaction rate (with respect to the control experiment) quite significant, especially in the case of compound **15** (entry 5). There is also a general trend to increase the yield of *exo* (*cis*) isomers in favour of the *endo* (*trans*) isomers. This is similar to what it was observed for the gold(III) complexes depicted in Table 1. Nevertheless, and as it occurred in the control experiment, isomer **3d** is not obtained with any of the gold(III) catalysts tested.

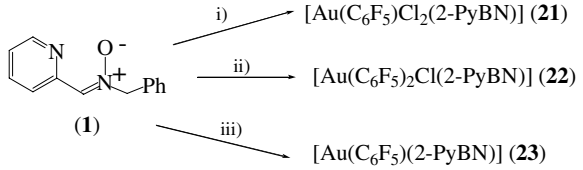
It appears that the active catalytic species could be gold(III) anions of the type [AuCl$_4$]$^-$, anionic species such as [AuRCl$_3$]$^-$ or [AuR$_2$Cl$_2$]$^-$ (R = mes, C_6F_5) and the neutral species [Au(C_6F_5)Cl$_2$(tht)] (analogous to [Au(C_6F_5)Cl$_2$]$_2$ but isolable). All these species could coordinate, in the reaction conditions, nitrone (**1**) or methyl acrylate (**2**) molecules to the gold(III) centre.

Organometallic gold(I) complexes with the C_6F_5 or mes radicals, can be used in the cycloaddition reaction. Considering that one requirement for this catalysis is the presence of an Au–Cl bond, we have chosen ionic derivatives of the type PPN[AuRCl] with R = mes, **18**, C_6F_5, **19**. In these cases (Table 3) only a reduction of the time reaction was found, while the relation *endo*/*exo* is practically unchanged.

In order to determine the possible intermediates of the cycloaddition reaction, as confirmed in the case of zinc and silver derivatives, [4] we performed the reaction between the nitrone **1** and some of the organometallic gold(III) and gold(I) complexes (Scheme 1).

As starting gold(III) derivatives with the pentafluorophenyl radical, we used complexes [Au(C_6F_5)Cl$_2$(tht)] (**15**) and [Au(C_6F_5)$_2$Cl]$_2$ (**16**), which had the labile tht ligand or that were dimers that could react easily with **1**. In the first case labile tht is displaced by the nitrone **1** giving rise to complex **21**, whose spectroscopic data point to a coordination of **1** to the metallic centre through the oxygen atom. Thus, the ^{1}H NMR spectrum displays a downfield displacement of the nitrone resonances (mainly for δ (HC=N) and δ (NCH$_2$Ph) resonances) as occurred in silver and zinc complexes described previously by us [3,4]. The ^{19}F NMR spectrum exhibits a characteristic pattern for a square-planar gold(III) complex [6].

In the case of compound [Au(C_6F_5)$_2$Cl]$_2$ (**16**), the isolated complex **22**, shows a similar ^{1}H NMR spectrum than that of **21**; however, the ^{19}F NMR spectrum at room temperature displays six resonances, as expected for a *cis*-pentafluorophenyl complex. Some of these signals are broad and not totally resolved, indicating that one of the C_6F_5 ring does not have a free rotation. The spectrum at −60 °C confirms this assumption and shows how the broad signals that appear at −124.0 ppm



i) [Au(C_6F_5)Cl$_2$(tht)], ii)[Au(C_6F_5)$_2$Cl]$_2$, iii) [Au(C_6F_5)(tht)]

Scheme 1.

Table 3
Catalytic activity of organometallic gold(III) and gold(I) compounds and complexes in the 1,3-cycloaddition reaction of **1** and **2**

Entry	Compound	Catalyst (mol%)	Isomers (%) *endo*/*exo*	Time (h)	Conversion (%)[a]
1	PPN[Au(mes)Cl$_3$] (**11**)	10	58/42	84	100
2	PPN[Au(C_6F_5)Cl$_3$] (**12**)	10	55/45	60	100
3	*cis*-PPN[Au(mes)$_2$Cl$_2$] (**13**)	10	55/45	92	100
4	*trans*-NBu$_4$ [Au(C_6F_5)$_2$Cl$_2$] (**14**)	10	60/40	78	100
5	[Au(C_6F_5)Cl$_2$(tht)] (**15**)	10	53/47	48	100
6	[Au(C_6F_5)$_2$Cl]$_2$ (**16**)	10	77/23	90	100
7	[Au(mes)$_2$Cl]$_2$ (**17**)	10	56/44	72	100
8	PPN[Au(mes)Cl] (**18**)	10	66/34	48	100
9	PPN[Au(C_6F_5)Cl] (**19**)	10	66/34	72	100

[a] Conversion and selectivity measured by ^{1}H NMR (CDCl$_3$).

at room temperature (and that correspond to the F*ortho*) split in two resonances at −123.1 and −125.6 ppm. Besides, there is a better resolution for the signals that correspond to the F*meta* and F*para* (see Section 3).

Reactions of nitrone **1** with gold(III) complexes containing the organic ligand mesityl $[Au(mes)_2Cl]_2$ afforded mixtures of unidentified and more complicated compounds that are currently under investigation.

Complex $[Au(C_6F_5)(tht)]$ (**20**) was chosen as a gold(I) organometallic starting material. The reaction with the nitrone, **1** (Scheme 1, *iii*) afforded the stable complex **23**, as a result of the displacement of tht by the nitrone. All spectroscopic data (see Section 3) point to the coordination of the nitrone to the metallic centre (through the O-atom) giving rise to a gold(I) linear compound.

Once the nitrone-complexes (**21–23**) were synthesized we carried out the stoichiometric 1,3-cycloaddition reaction with methyl acrylate (**2**), to study their behaviour as possible metallic intermediates. However, the above mentioned reaction (same reaction conditions as that of analogous zinc and silver complexes [4]) gave no cycloaddition products. Decomposition to metallic gold as a consequence of reduction from gold(III) and gold(I) to gold(0) was observed instead in all cases.

Compounds **21**–**23** were also tested in the cycloaddition reaction between 2-PyBN (**1**) and methyl acrylate (**2**), Eq. (1), in catalytic amounts (10 mol%). The results are collected in Table 4. There is only a significant increase of the reaction rate in the case of compound **21** $[Au(C_6F_5)Cl_2(2\text{-PyBN})]$ which has got two chloride atoms coordinated to the metallic centre (Table 4, entry 1). In the case of the gold(III) compound $[Au(C_6F_5)_2Cl(2\text{-PyBN})]$, **22**, with two coordinated pentafluorophenyl groups or the gold(I) complex $[Au(C_6F_5)(2\text{-PyBN})]$, **23**, the increase is not very high or else, the reaction rate is decreased (entry 2) in comparison to the control experiment. Nevertheless, a moderate regioselectivity is observed with these novel compounds. The latter results point to the fact that the coordination of the nitrone to the gold(III) centre may not be the first step in the 1,3-cycloaddition reaction. Plausibly the first step should be the coordination of methyl acrylate (**2**) to the gold(III) or gold(I) centres (after the Au–Cl bond break-down under reaction conditions). However, this coordination may give rise to very reactive vinyl complexes that coordinate subsequently the nitrone (**1**) and give the 1,3-cycloaddition reaction as we have not been able to isolate stable gold-alkene intermediates. Some gold(I)-alkene derivatives have been reported on the past [9] as well as gold(III) and gold(I) vinyl complexes [6,10]. However, the reactions of gold(III) and gold(I) compounds with unsaturated reagents lead usually to quite unstable species [6].

To summarize we have shown that gold(III) and gold(I) coordination compounds as well as organometallic derivatives are able to catalyze the 1,3-dipolar cycloaddition reaction of N-benzyl-C(2-pyridyl) nitrone and methyl acrylate decreasing the reaction time and favouring the formation of the *exo* (cis) isomer. It seems that the first step in this reaction could be the cleavage of a Au–Cl or $Au–C_6F_5$ bond and subsequent coordination of the methyl acrylate, giving rise to reactive intermediates towards the 2-PyBN nitrone to afford the cycloaddition products. The reaction of $[AuCl_3(tht)]$ with 2-PyBN unexpectedly affords the ionic compound [2-PyBN–H][$AuCl_4$] (**5**) whose crystal structure has been confirmed by X-ray studies. The catalytic activity and moderate regioselectivity displayed by this compound has helped us to find analogous (and more active) gold(III) and gold(I) inorganic and organometallic catalysts, although the action mechanism of the later could be different of the former (**5**). Novel nitrone gold(III) and gold(I) complexes have been prepared and fully characterized. From their lack of reaction with methyl acrylate to give cycloaddition products and their low catalytic activity, we conclude that they are not plausible intermediates in the 1,3-dipolar cycloaddition reaction (as opposed to what it was found for analogous Ag(I) and Zn(II) nitrone derivatives in our previous investigations). Reactions of gold complexes with nitrones and cycloaddition reactions of nitrones with different dipolarophiles (catalysed by gold complexes) are currently under investigation by our research group.

3. Experimental

3.1. General procedures

IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^1H-, ^{13}C- and ^{19}F NMR spectra were recorded on a Varian UNITY 200 or 300 or BRUKER 300 in $CDCl_3$ or

Table 4
Catalytic activity of novel organometallic nitrone gold(III) and gold(I) compounds in the 1,3-cycloaddition reaction of **1** and **2**

Entry	Compound	Catalyst (mol%)	Isomers (%) *endo*/*exo*	Time (h)	Conversion (%)[a]
1	$[Au(C_6F_5)Cl_2(2\text{-PyBN})]$ (**21**)	10	61/39	72	100
2	$[Au(C_6F_5)_2Cl(2\text{-PyBN})]$ (**22**)	10	65/35	120	100
3	$[Au(C_6F_5)(2\text{-PyBN})]$ (**23**)	10	60/40	84	100

[a] Conversion and selectivity measured by ^1H NMR ($CDCl_3$).

$(CD_3)_2CO$ solutions; chemical shifts are quoted relative to $SiMe_4$ (^1H, ^{13}C), and $CFCl_3$ (external ^{19}F). The C, H, N analyses were performed with a Perkin–Elmer 2400 microanalyser. 2-PyBN (**1**) [11]; PPN[$AuCl_2$] (**9**) [12]; [AuCl(tht)] (**10**) [13]; PPN[Au(mes)Cl_3] (**11**) [14]; PPN-[Au(C_6F_5)Cl_3] (**12**) [15]; *cis*-PPN[Au(mes)$_2Cl_2$] (**13**) [6,16]; *trans*-NBu_4[Au(C_6F_5)$_2Cl_2$] (**14**) [17]; [Au(C_6F_5)Cl_2(tht)] (**15**) [18]; [Au(C_6F_5)$_2Cl]_2$ (**16**) [19]; [Au(mes)$_2Cl]_2$ (**17**) [16]; PPN[Au(mes)Cl] (**18**) [14], PPN[Au(C_6F_5)Cl] (**19**) [20]; and [Au(C_6F_5)(tht)] (**20**) [21] were prepared by established procedures. Methyl acrylate (**2**) was purchased from Aldrich whereas Na[$AuCl_4$] (**7**) was a commercial product from Kemplate España S.A. [$AuCl_3$(tht)] (**4**), and PPN[$AuCl_4$] (**8**) were prepared by oxidative addition of [AuCl(tht)] (**10**) or PPN[$AuCl_2$] (**9**) with $PhCl_2I$ (in a 1:1 molar ratio).

3.2. Synthesis

3.2.1. Synthesis of [2-PyBN–H][$AuCl_4$] (**5**) (Eq. (2))

To a solution of [$AuCl_3$(tht)] (**4**) (0.039 g, 0.1 mmol) in dichloromethane (20 ml) was added 2-PyBN (**1**) (0.021 g, 0.1 mmol) and the mixture was stirred at room temperature for 1.5 h. The solution was concentrated in vacuum to 3 ml. leading to the precipitation of **5** as a yellow solid which was washed with diethyl ether and dried in vacuum. Yield (%): 76. Anal. Calc. for $C_{13}H_{13}N_2OAuCl_4$: C, 26.10; H, 2.37; N: 5.09. Found for **5**: C, 26.49; H, 2.36; N, 4.91%. IR (cm^{-1}, Nujol): ν(C=N) = 1594 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 16.5 (s, br, 1H, N–*H*), 9.22 (d, 1H, H_4, $J = 5.7$ Hz), 9.08 (s, 1H, *H*C=N), 8.96 (td, 1H, H_2, $J = 7.8$ Hz, $J = 1.2$ Hz), 8.45 (d, 1H, H_3, $J = 7.8$ Hz), 8.42 (t, 1H, H_1, $J = 1.2$ Hz), 7.5 (m, 2H, H_5, H_9), 7.57 (m, 3H, H_6, H_7, H_8), 5.61 (s, 2H, NCH_2–Ph). ^{13}C NMR($(CD_3)_2CO$): δ 147,0; 140.6; 133.0; 130.1; 129.7; 129.1; 128.8; 128.7; 127.8; 71.7.

3.2.2. Synthesis of [2-PyBN–H][TfO] (**6**) (Eq. (3))

To a solution of 2-PyBN (**1**) (0.042 g, 0.2 mmol) in 20 ml of dichloromethane, 18 μl of triflic acid (HCF_3SO_3, HTfO) was added. The mixture was stirred at room temperature during 2 h. Subsequent removal of the solvent (to ca. 5 ml) and addition of a mixture of diethyl ether and *n*-hexane (20 ml) led to the precipitation of **6** as a white solid which was filtered off and vacuum dried. Yield (%): 45. Anal. Calc. for $C_{14}H_{13}O_4F_3N_2S$: C, 46.41; H, 3.62; N 7.73%. Found for **6**: C, 46.01; H, 3.38; N, 7.58%. IR (cm^{-1}, Nujol): ν (C=N) = 1563 cm^{-1}, ($SO_3CF_3^-$), 1281 (vs, br), 1225 (s), 1154 (s). ^1H NMR ($(CD_3)_2CO$): δ 16.4 (s, br, 1H, N-*H*), 9.05 (d, 1H, H_4, $J = 5.1$ Hz), 9.01 (s, 1H, *H*C=N), 8.79 (td, 1H, H_2, $J = 8.4$ Hz, $J = 1.5$ Hz), 8.29 (d, 1H, H_3, $J = 8.7$ Hz), 8.27 (td, 1H, H_1, $J = 8.3$, J = 4.8 Hz), 7.60 (m, 2H, H_5, H_9), 7.40 (m, 3H, H_6, H_7, H_8), 5.42 (s, 2H, NCH_2–Ph).

3.2.3. Synthesis of [Au(C_6F_5)Cl_2(2-PyBN)] (**21**) (Scheme 1)

To a solution of [Au(C_6F_5)Cl_2(tht)] (**15**) (0.052 g, 0.1 mmol) in dichloromethane (20 ml) was added 2-PyBN (**1**) (0.021 g, 0.1 mmol). The mixture was stirred at room temperature for 1.5 h. Removal of the solvent to ca. 5 ml and addition of *n*-hexane (20 ml) afforded **21** as a white solid that was subsequently filtered off and vacuum dried. Yield (%): 77. Anal. Calc. for $C_{19}H_{12}N_2O$ $AuCl_2F_5$: C, 35.26; H, 1.87; N 4.33%. Found for **21**: C, 35.36; H, 2.03; N, 3.92%. IR (cm^{-1}, Nujol): ν (C=N) = 1562 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.43 (d, 1H, H_4), 8.75 (d, 1H, H_1), 7.63 (s, br, 1H, H_3), 8.11 (t, 1H, H_2) 7.92 (s, 1H, *H*C=N), 7.50 (m, 2H, H_5, H_9), 7.40 (m, 3H, H_6, H_7, H_8), 5.22 (s, 2H, N–CH_2–Ph). ^{19}F NMR ($CDCl_3$): δ: −125.22 (dd, br, 2F, F_o), −155.31 (t, ^1F, F_p), −161.10 (t, 2F, F_m). ^{13}C NMR ($CDCl_3$): δ 149.7, 137.3, 135.8, 133.0, 124.7, 124.1, 72.1. LSIMS$^+$: m/z (%) = 611 (78%, $[M–Cl]^+$, 576 (46%, $[M–2Cl]^+$), 409 (100%, [Au–2PyBN]$^+$), 364 (88%, [AuC_6F_5]).

3.2.4. Synthesis of [Au(C_6F_5)$_2$Cl(2-PyBN)] (**22**) (Scheme 1)

To a solution of [Au(C_6F_5)$_2Cl]_2$ (**16**) (0.056 g, 0.1 mmol) in dichloromethane (20 ml) was added 2-PyBN (**1**) (0.021 g, 0.1 mmol). The mixture was stirred at room temperature for 30 min and concentrated to ca. 5 ml. Addition of *n*-hexane (20 ml) led to the isolation of **22** as a white solid. Yield (%): 58. Anal. Calc. for $C_{25}H_{12}N_2OAuClF_{10}$: C, 38.55; H, 1.55; N 3.59%. Found for **22**: C, 38.70; H, 1.67; N, 3.70%. IR (cm^{-1}, Nujol): ν (C=N) = 1557 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.43 (d,1H, H_4), 8.77 (s, 1H, *H*C=N), 8.71 (d, 1H, H_1), 8.06 (t, 1H, H_2), 7.60 (s, br, 1H, H_3), 7.57 (m, 2H, H_5, H_9), 7.44 (m, 3H, H_6, H_7, H_8), 5.22 (s, 2H, N–CH_2–Ph). ^{19}F NMR ($CDCl_3$, 25 °C): δ: −123.1 (m, 2F, F_o) −124.5 (m, vbr, 2F, F_o), −153.6 (t, 1F, F_p), −155.3 (t, 1F, F_p), −159.2 (m, 2F, F_m), −160.8 (m, br, 2F, F_m). ^{19}F NMR ($CDCl_3$, −60 °C): δ: −123.17 (s, 1F, F_o), −123.47 (s, 2F, F_o), −125.67 (s, 1F, F_o) −152.65 (t, 2F, F_p), −154.31 (t, 2F, F_p), −158.40 (dt, 4F, F_m), −159.94 (dt, 4F, F_m). ^{13}C NMR ($CDCl_3$): δ 149.6, 148.2, 141.9, 131.9, 130.1, 129.9, 129.6, 129.1, 127.2, 127.0, 74.3. LSIMS$^+$: m/z (%) = 743 (100%, $[M–Cl]^+$), 409 (47%, [Au–(2PyBN)]$^+$).

3.2.5. Synthesis of [Au(C_6F_5)(2-PyBN)] (**23**) (Scheme 1)

To a solution of [Au(C_6F_5)(tht)] (**20**) (0.045 g, 0.1 mmol) in dichloromethane (20 ml) was added a solution of 2-PyBN (**1**) (0.021 g, 0.1 mmol). After 1.5 h stirring at room temperature the reaction mixture was concentrated to ca. 3 ml. The addition of diethyl ether (10 ml) afforded **23** as a white solid that was further filtered off and vacuum dried. Yield (%): 52. Anal. Calc. for $C_{19}H_{12}N_2OAuF_5$: C, 39.60; H, 2.09; N 4.86%. Found for **23**: C, 40.05; H, 1.85; N, 4.48%. IR (cm^{-1}, Nujol): ν

(C=N) = 1596 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.43 (d,1H, H_4), 8.96 (s, 1H, *H*C=N), 8.70 (d, 1H, H_1), 8.07 (t, 1H, H_2), 7.54 (s, br, 1H, H_3), 7.57 (m, 2H, H_5, H_9), 8.47 (m, 3H, H_6, H_7, H_8), 5.14 (s, 2H, N–CH_2–Ph). ^{19}F NMR ($CDCl_3$): −118.25 (dd, br, 2F, F_o), −161.12 (t, 1F, F_p), −169.94 (t, 2F, F_m). ^{13}C NMR ($CDCl_3$): δ 151.46, 149.05, 140.00, 131.77, 131,14, 129.63, 129,63, 129,19, 125.68, 73.19. LSIMS$^+$: m/z (%) = 576 (97%, $[M]^+$), 409 (93%, $[M–C_6F_5]^+$), 743 (33%, {Au[(C_6F_5)(2-Py-BN)]$_2$}) 1153 (17%, [Au(C_6F_5)(2-PyBN)]$_2$).

3.3. Crystal structure determination of compound 5

Single crystals were grown by diffusing diethyl ether into an acetone solution of complex [2-PyBN–H][$AuCl_4$] (**5**) mounted on a glass fibre using the inert oil technique. Crystals of **5** were mounted on a glass fibre on a Bruker–Siemens Smart CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$) with a nominal crystal to detector distance of 4.0 cm.

3.3.1. Crystal data and data collection parameters

5$C_{13}H_{13}AuCl_4N_2O$, $M = 552.02$, Monoclinic, $a = 11.280(3)$, $b = 10.304(2)$, $c = 14.238(3)$ Å, $\beta = 99.236(3)°$. $V = 1633.4(6)$ Å^3, $T = 150$ K, space group $P2(1)/n$, graphite monochromated Mo Kα radiation, $\lambda = 0.71069$ Å. $Z = 4$, $D_{cal} = 2.245$ mg m^{-3}, $F(0\,0\,0) = 1040$, colourless prism with dimensions $0.39 \times 0.14 \times 0.079$ mm, $\mu = 9.659$ mm^{-1}, θ range for data collection 2.14–27.02°, $-10 \leqslant h \leqslant 14$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 18$; 10016 reflections collected, 3546 independent ($R_{int} = 0.0291$).

3.3.2. Structure solution and refinement

The structure was solved by direct methods (SHELXS97) [21] and refined by full-matrix least-squares on F^2, using the program SHELXL97 [22]. All data were corrected using the program SADABS [23]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement proceeded to: $R = 0.0227$, $wR = 0.0652$ for 195 parameters, and $R = 0.0244$, $wR = 0.0660$ for all data, electron density fluctuates in the range 1.254 and −1.150 e Å^{-3}.

3.4. Standard catalytic procedure

To a solution of 2-PyBN (**1**) (0.025 g, 0.1125 mmol) in acetone (20 ml) methylacrilate (**2**) (0.106 ml, 1.125 mmol) and the amount of gold catalyst specified in Tables 1 and 3 were added. The reaction mixture was refluxed and aliquots were taken at different reaction times (after cooling down the mixture at room temperature). The solvent from the aliquots was completely removed and the crude residue was analysed by ^1H NMR ($CDCl_3$). The products ratio **3a**:**3b**:**3c** could be established unambiguously by NMR although the crude material can be purified by PCAR-TCL using a Chromatotron (2 mm layer thickness) as described previously [3].

4. Supplementary material

Tables of thermal parameters and observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre. Any request for this material should quote a full literature citation and the reference number CCDC 218856 and may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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