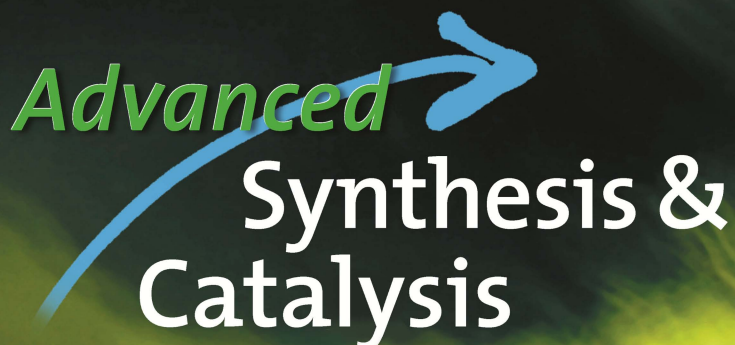


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Oxidation State and Halogen Influence on the NHC-Gold-Halide-Catalyzed Cyclization of Propargylic Amides

Nicola Sargentoni,^a Rossana Galassi,^{*a} Lorenzo Luciani,^a Frank Rominger,^b Matthias Rudolph,^b A. Stephen K. Hashmi^{*b}

^a School of Science and Technology, Chemistry Division, University of Camerino, Via Madonna delle Carceri, I-62032, Italy

^b Organisch-Chemisches Institut, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

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Abstract. The homogeneously catalyzed cycloisomerization reaction of propargylic amides was tested as benchmark reaction for two homologous series of Au(I) and Au(III) complexes with NHC ligands. This reaction is known to afford either aromatic oxazoles or dihydrooxazoles, depending on the oxidation state of the applied gold catalysts. For this purpose, symmetric and unsymmetric NHC ligands with mixed alkyl or benzyl substituents (1,3-dimethylimidazolyl-2-yl or 1-benzyl-3-methylimidazolyl-2-yl) and the corresponding Au(I) and Au(III) derivatives were prepared and characterized by analytical methods, IR and ¹H and ¹³C NMR spectroscopies, and by X-ray diffraction methods.

Ten NHC-gold(I) and NHC-gold(III) complexes were tested on the cyclization reactions by adding gold catalysts in the presence and absence of AgPF₆. Noteworthy, only the 1-benzyl-3-methyl-gold(III) trichloride was able to give selectively the aromatic oxazole without the addition of the silver salt. Interestingly, on contrary to what is reported in the literature, the use of gold(I) or gold(III) complexes does not influence the chemoselectivity of the cyclization reaction, while the halide bound to the metal does. In this regard, a mechanism purposing the dihydrooxazole as an intermediate for the formation of aromatic oxazole is proposed.

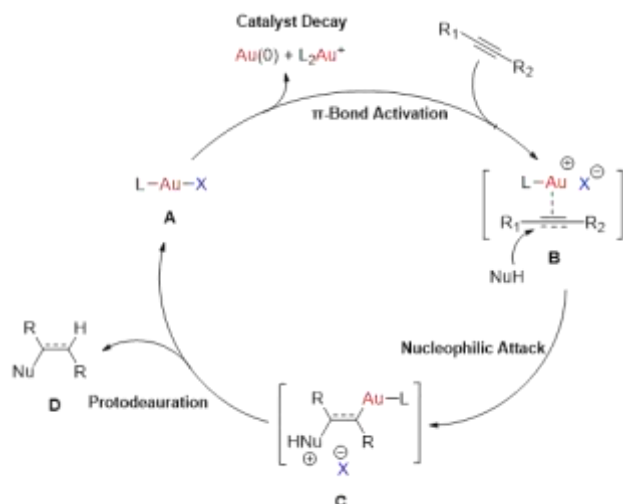
Keywords: gold, catalysis, cyclization, oxidation state, NHC gold complexes, Au(I), Au(III)

Introduction

Over the last decades, gold catalysis has become a robust synthetic method to approach many organic transformations.^[1] Due to their unique π -affinity, gold(I) and gold(III) catalysts are mostly applied for the activation of carbon-carbon π -bonds (alkynes, allenes, alkenes) towards nucleophilic attack.^[2] As a general mechanism, the gold metal fragment (**A**) acts as a π -acid, coordinating unsaturated hydrocarbons (intermediate **B**, Scheme 1). Subsequently, these coordinated hydrocarbons undergo nucleophilic attack by a nucleophile (NuH), leading to the formation of organogold intermediate **C**. The gold-carbon bond is typically cleaved through protonation (protodeauration), resulting in the desired product (**D**) under the regeneration of the catalyst **A**. Multiple factors can impact these stages of gold-catalysed reactions, potentially diminishing the overall efficiency of the reaction. Primarily, optimizing catalytic efficiency involves fine-tuning of the catalyst **A** itself through modifications to both the ligand (L)

and the counter anion (X^-).^[3] Indeed, the effects of both ligand and counter anion are considered fundamental factors in homogeneous gold catalysis.^[4] In this context, N-heterocyclic carbenes (NHCs) have demonstrated to be ideal ancillary ligands in combination with gold. The stereo-electronic properties of both NHC-gold(I)X and gold(III)X₃ complexes (X = Cl, Br or I) can be modulated by changing the carbene structure or the substituents at the N-positions.^[5] On the other hand, despite being usually regarded as innocent partners, the metal counter anions, for example halides (Cl⁻, Br⁻, and I⁻), also proved to be highly influential in both the reaction mechanism and the regioselectivity.^[6] From a mechanistic standpoint, gold catalysis involves the association/dissociation of counter anions from the cationic gold center^[7] and the affinity between gold and the counter anion is crucial since a high affinity implies a high energy barrier to overcome, thereby impeding the efficiency of the catalytic cycle.^[8] Additionally, proton transfer in a reaction is another significant factor and counter anions are more likely to act as hydrogen-bond acceptors with the proton,

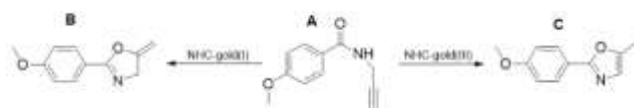
influencing the overall reaction rate and subsequently augmenting the nucleophilicity of the attacking nucleophile.^[9] Furthermore, the stability of gold catalysts has been found to be influenced by their counterions.^[10]



Scheme 1. Simplified gold catalysis cycle.

Moreover, the oxidation state of the gold center has a significant influence on the regioselectivity as well as switching from gold(I) to gold(III) may have extreme outcomes, even leading to different reaction products.^[11] A rational understanding of all these factors is still lacking and uncertainties exist regarding the actual importance of the oxidation state of the catalytic species since the presence of a highly donating counter anion, more than the oxidation state,^[12] seems to be responsible for the observed selectivity.

Thus, in this work, the influence of both the oxidation state and the nature of the halogen at the gold(I/III) center were considered with regard to the gold oxidation-state-dependent cycloisomerization of 4-methoxy-N-(prop-2-yn-1-yl)benzamide (**A**) to 2-(4-methoxyphenyl)-5-methylene-4,5-dihydrooxazole (**B**) or 2-(4-methoxyphenyl)-5-methyloxazole (**C**) (Scheme 2).^[13]



Scheme 2. The cyclization of N-propargyl carboxamide is the benchmark reaction to test the gold catalysts in this work.

Starting from 1,3-dimethyl-NHC-gold(I) chloride and 1-benzyl-3-methyl-NHC-gold(I) chloride, metathesis reactions with sodium iodide or sodium bromide provided NHC-Au(I)X species. Their oxidation to the corresponding NHC-Au(III)X₃ complexes (X = Cl, Br or I) were also performed. All complexes were isolated as single crystals and characterized by elemental analysis, ¹H and ¹³C NMR, IR-ATR spectroscopy and single crystal X-ray diffraction. Finally, the catalytic behaviour of these complexes was studied for the cyclization reaction of the N-propargyl carboxamide.

Results and Discussion

Synthesis of complexes

The elegant one-pot “weak base” route,^[14] involving imidazolium salts and gold precursors ([AuCl(Me₂S)] (Me₂S = dimethyl sulfide) or [AuCl(tht)] (tht = tetrahydrothiophene) in the presence of a mild base, such as K₂CO₃, was employed for the synthesis of 1,3-dimethyl-imidazolyl-2-yl-gold(I) chloride (**1-Cl**) and 1-benzyl-3-methyl-imidazolyl-2-yl-gold(I) chloride (**2-Cl**). Both **1-Cl** and **2-Cl** have been identified as mono-carbene species by X-ray crystal structure determinations. While the molecular structure of **1-Cl** has already been reported in the literature,^[15] **2-Cl** is discussed in this work (see *infra*). Both compounds, **1-Cl** and **2-Cl**, are rather stable in solution as highlighted by the analysis of the ¹H and ¹³C NMR spectra (see Figure 1-5S in Supporting Information). NMR data are in accordance with those reported in the literature.^[16-19]

The preparation of the corresponding gold(III) complexes **1-Cl₃** and **2-Cl₃** was achieved by adding PhICl₂ (pathway A in Schemes 3 and 4).^{[20],[21]} The ¹H NMR spectra in deuterated acetonitrile are reported in Figure 6S and 8S in SI, displaying the expected very clean patterns of peaks. The oxidation of the central metal slightly affects the chemical shifts of both methyl and imidazole protons in the ¹H NMR. From **1-Cl** to **1-Cl₃**, variations of +0.02 ppm for the methyl resonance and of +0.13 ppm for the imidazole protons were observed. Similarly, in the ¹³C NMR spectra only slight shifts are recorded for both the methyl and the N-C-C-N resonances while the carbene NCN carbon was found to be stronger influenced by the change of the oxidation state with a -23.65 ppm shift (from 170.65 ppm in **1-Cl** to 147 ppm in **1-Cl₃**, see Figure 7S and 9S in SI). The oxidation of **2-Cl** to **2-Cl₃** led to higher chemical shift in respect to **1-Cl₃**; in the ¹H NMR spectrum, a +0.11 ppm and +0.20 ppm shift deviation was observed for the methyl and the imidazole protons, respectively. Finally, the ¹³C NMR spectrum of **2-Cl₃** shows the expected shift of the NCN resonance, from 170.23 ppm for **2-Cl** to 138.97 ppm for **2-Cl₃**. ¹³C NMR is a powerful analytical tool for the study of NHCs and a great upshift of the carbene NCN carbon is attained switching from NHC-gold(I) to NHC-gold(III)^{[20],[22]} and can be considered diagnostic for the oxidation of the Au(I) compounds. The mono-carbene nature of **1-Cl₃** and **2-Cl₃** compounds was unambiguously assigned by X-ray crystal structure determination (see below).

Complex [(NHC)₂Au](AuBr₂) (**1_{bis}-AuBr₂**) (pathway B, Scheme 3) was obtained in a 74% yield by treating **1-Cl** with a large amount of sodium bromide (24 hours at room temperature, in accordance with a slightly modified procedure reported in the literature).^[23] The substitution of chloride with bromide ion facilitates the ligands scrambling with the formation of the relative bis-carbene species and AuBr₂⁻ as counterion, as evidenced by the resolution of the X-ray diffraction crystal structure determination (*vide infra*). Conversely, the metathesis of complex **2-Cl** with an

excess of sodium bromide affords the mono-carbene **2-Br** in a 91% yield (pathway **C**, Scheme 4) highlighting the significant role of the benzyl vs methyl substituents at the imidazole ring. Both in-solution and solid-state characterizations of **2-Br**, including the X-ray structure determination, agreed with those already reported in the literature.^[24]

The mono-carbene derivatives **1-Br₃** and **2-Br₃** were obtained by oxidation with a slight excess of elemental bromine in acetonitrile at room temperature.^[25] Both compounds were obtained in high yields (93% for **1-Br₃** and 84% for **2-Br₃**, pathway **D** and pathway **E** in Schemes 3 and 4, respectively). **2-Br₃** resulted to be a mono-carbene with the AuBr₃-moiety similarly to the **1-Br₃** (*vide infra*); the formation of the monocarbene **1-Br₃** highlights that the oxidation process of **1-Br** necessarily involves ligand exchange and further rearrangements. In the ¹H NMR spectrum, the oxidation of the metal centre of **2-Br** leads to only slight ¹H NMR shifts for both methyl and imidazole proton resonances, while the largest effects are recorded for the NCN signals in the ¹³C NMR spectra; in fact, shifts of -37 ppm and -26 ppm were observed from **1_{bis}-AuBr₂** to **1-Br₃** and from **2-Br** to **2-Br₃**, respectively. Significant distinctions may emerge in the ¹³C NMR spectra between neutral and ionic gold complexes. In cationic bis-carbene complexes of the [(NHC)₂Au]⁺ type, the positive charge on the gold atom causes a significant shift to higher frequencies in the ¹³C NMR spectrum, for the [(1-benzyl-3-methyl-NHC)₂Au][AuBr₂]^[24] the NCN peak falls at 186.4 ppm, while the mono-carbene 1-benzyl-3-methyl-NHC-AuBr (**2-Br** in this work) is at 172.7 ppm.^[24]

The metathesis reaction of complex **1-Cl** with sodium iodide led to the isolation of the bis-carbene species [(NHC)₂Au](AuI₂) (**1_{bis}-I**) in a 43% yield (pathway **F**, Scheme 3).^[26a]

By considering the better solubility of **2-Cl**, the metathesis reaction with an excess of sodium iodide was conducted in acetonitrile,^[26b] yielding the bis-carbene complex **2_{bis}-I** (pathway **G**, Scheme 4) in a better yield (68%) compared to **1_{bis}-I**. As above mentioned, the bis-carbene nature of these compounds was highlighted by X-ray diffraction molecular structure determinations and by the chemical shifts of the NCN signals in the ¹³C NMR spectra (180 ppm in CD₃CN for **1_{bis}-I** and 180.45 for **2_{bis}-I**, Figure 19S and 21S respectively).

All the ¹³C NMR data of the herein discussed compounds are reported in Table 1. The analysis of the chemical shifts individuates trends which are due to the oxidation of the metal centre as well as the nature of the trans ligand to the NCN carbon. In detail, the ¹³C NMR resonances are the most diagnostic data to evaluate the oxidation at the gold centre. In fact, complexes **1-Cl₃** and **1-Br₃** showed the typical imidazolyl NCN-upshift at, respectively, 147.00 and 136.60 ppm, with respect to the starting NHC-gold(I) **1-Cl** and (NHC)₂-gold(I) **1_{bis}-AuBr₂** complexes at 170.65 and 173.62 ppm, respectively.

Table 1. ¹³C NMR chemical shifts for the NCN imidazolyl carbon atom for all the Au(I) and Au(III) complexes recorded in d³-acetonitrile.

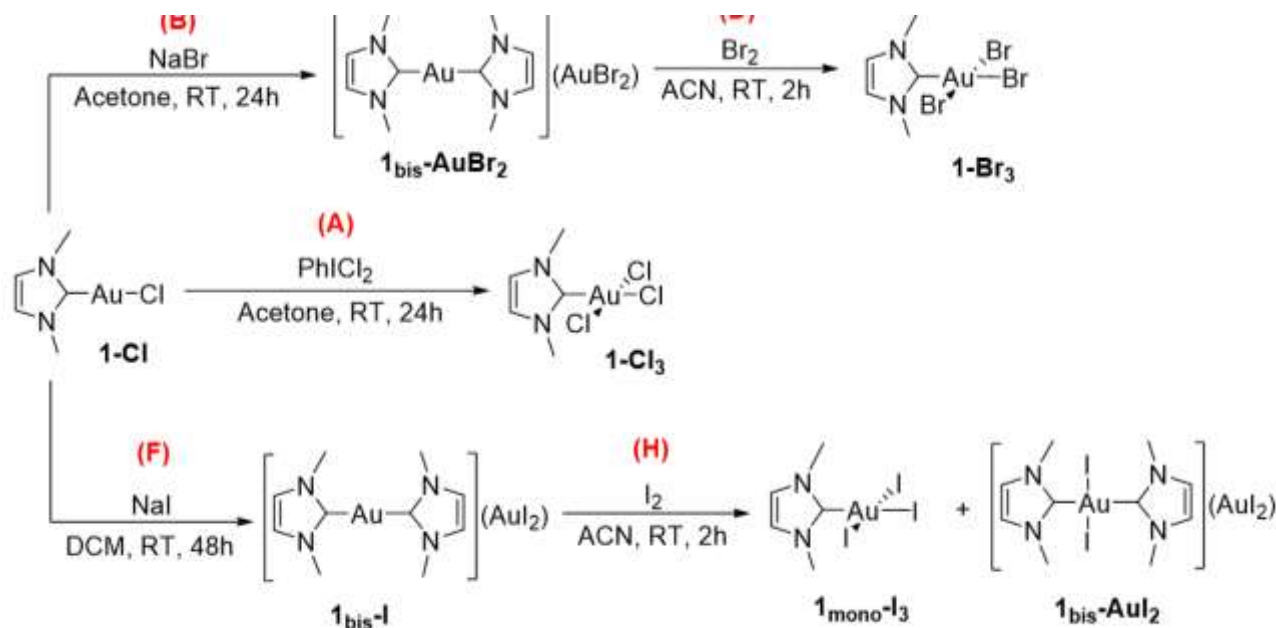
Compounds	¹³ C NMR Chemical Shift (ppm)
1-Cl	170.65 ^a
1-Cl₃	147
1_{bis}-AuBr₂	174.05
1-Br₃	136.63
1_{bis}-I	180.93
1_{mono}-I₃ / 1_{bis}-AuI₂	144.63 (1_{bis}-AuI₂)
2-Cl	171.23
2-Cl₃	138.5
2-Br	173.63
2-Br₃	137.46
2_{bis}-I	180.45
2_{mono}-I₃	135.5
2_{bis}-I₃/AuI₄	144.97

^a) Data from the literature [12]

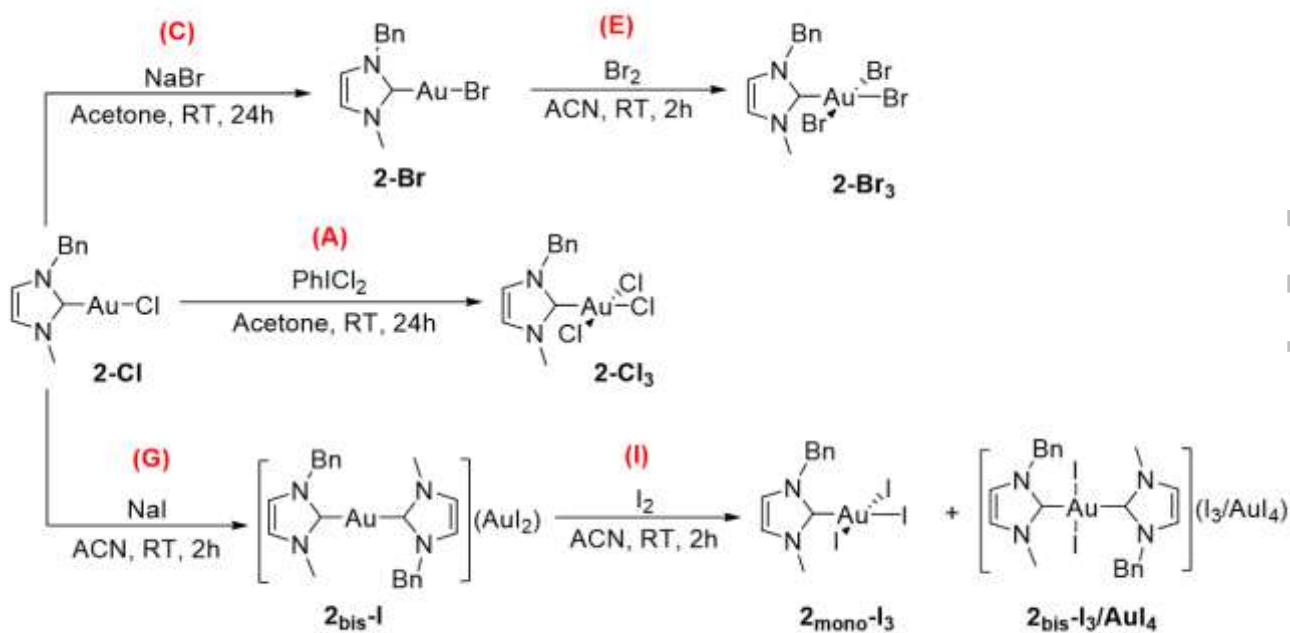
Beside these observations, by comparing analogous mono-carbene NHC-AuX species, for example the **2-Cl** and **2-Br**, an increase of the chemical shift (+ 2.63 ppm) is found while for the oxidized homologous series **2-Cl₃**, **2-Br₃** and **2_{mono}-I₃** an inverse trend is observed (X = Cl, 138 ppm, Br, 137, or I, 135 ppm). The trends herein observed agree with those reported in the literature for similar compounds.^[24]

With the aim to obtain the NHC-AuI₃ derivatives, the oxidation of **1_{bis}-I** and **2_{bis}-I** with solid iodine in acetonitrile at room temperature for 2 hours was considered. The oxidation of **1_{bis}-I** yielded a mixture of a mono and bis-carbene species namely 1,3-dimethyl-NHC-AuI₃ (**1_{mono}-I₃**) and [(1,3-dimethyl-NHC)₂AuI₂][AuI₂], **1_{bis}-AuI₂** (pathway **H**, Scheme 3). Similar results were reported by Weiss *et al.* by adopting different procedures.^[27] The oxidation of **2_{bis}-I** led to a mixture of 1-benzyl-3-methyl-NHC-AuI₃ (**2_{mono}-I₃**) and [(1-benzyl-3-methyl-NHC)₂AuI₂][I₃/AuI₄] (**2_{bis}-I₃/AuI₄**) species (pathway **I**, Scheme 4); indeed, from the reaction mixture, two different type of crystals were obtained whose X-ray crystal structure determination displayed the expected **2_{mono}-I₃** (see below), while a rather complicated composition was attained for the second type of crystal, where the co-existence of I₃⁻ and AuI₄⁻ as anions in the crystal unit for the [(1-benzyl-3-methyl-NHC)₂AuI₂], (**2_{bis}-I₃/AuI₄**) moiety was evidenced.

The elemental analysis of the microcrystalline powder agreed for a composition of the **2_{mono}-I₃**, **2_{bis}-I₃** and **2_{bis}-AuI₄** in a molar ratio of 4:1:1 confirmed by the integrals of the resonances in the ¹H NMR spectrum recorded in deuterated acetonitrile (see Figure 24S in SI). The ¹H NMR spectrum in CD₃CN of **2_{mono}-I₃**, **2_{bis}-I₃** and **2_{bis}-AuI₄** display three sets of signals which are coherent to the coexistence of mono and bis-carbene species. On the other hand, the ¹³C NMR spectrum of **1_{mono}-I₃** and **1_{bis}-AuI₂** (see Figure 23S in SI) did not



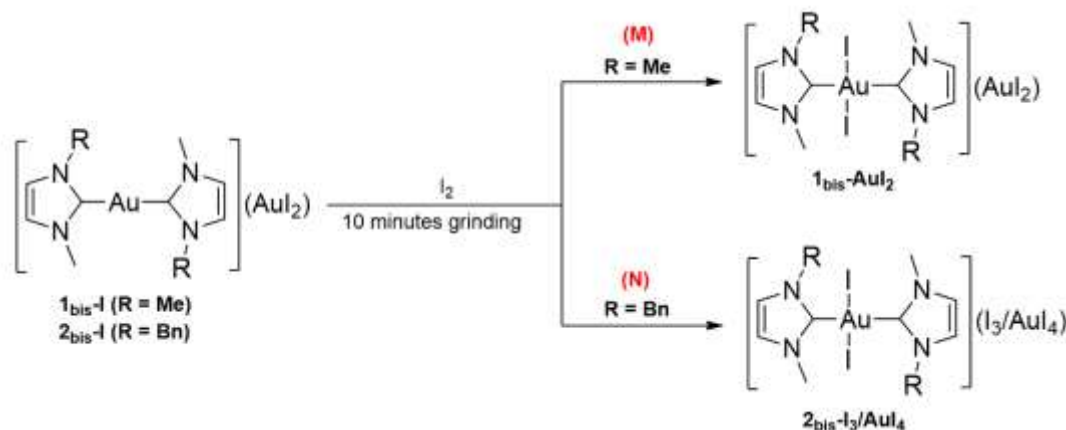
Scheme 3. Preparation of the 1-Cl series.



Scheme 4. Preparation of the 2-Cl series.

display the expected signals for the NCN atoms for both the mono and the bis-carbene species while the ^{13}C NMR spectrum acquired for the mixture $2_{\text{mono}}\text{-I}_3$ and $2_{\text{bis}}\text{-I}_3/\text{AuI}_4$ displays only a signal at 144.97 ppm for the bis-carbene derivatives independently from the counterion ($2_{\text{bis}}\text{-I}_3/\text{AuI}_4$) and a signal at 135.5 ppm for the NCN of $2_{\text{mono}}\text{-I}_3$ (see Table 1). These latter results led us to investigate the role of the solvent in the iodine oxidation reaction, given the well-known non-innocent behaviour of acetonitrile and the likely formation of small amounts of $[(\text{CH}_3\text{CN})_2\text{I}]_3$ in this solvent.^[12] To investigate this aspect, the solvent free

mechanochemical oxidation of 1_{bis}-I or 2_{bis}-I were attempted^[28] by using an apparatus consisting of a mortar and a pestle. Thus, 1_{bis}-I or 2_{bis}-I were grinded for 10 minutes without any solvent with an excess of solid iodine and, after grinding and selective washing with hexane, the formation of the bis-carbene species was observed, with varying counterions depending on the substituent pattern of the carbene ligands. $1_{\text{bis}}\text{-AuI}_2$ (pathway M, Scheme 5) or a mixture of $2_{\text{bis}}\text{-I}_3$ and $2_{\text{bis}}\text{-AuI}_4$ (pathway N, Scheme 5) were obtained by starting from 1_{bis}-I or 2_{bis}-I , respectively.



Scheme 5. Mechanochemical oxidation of $1_{\text{bis-I}}$ and $2_{\text{bis-I}}$ with solid iodine.

The absence of acetonitrile as solvent prevents the formation of $1_{\text{mono-I}_3}$ and $2_{\text{mono-I}_3}$ in the corresponding reactions. The slow conversion of the 1,3-dimethylimidazolyl-2yl-gold(I) chloride in acetonitrile to the corresponding bis-carbene was already reported in the literature.^[27] Conversely, the opposite trend is not documented. Herein, the ^1H NMR spectra of $1_{\text{bis-AuI}_2}$ or $2_{\text{bis-I}_3/\text{AuI}_4}$ clearly highlight the absence of the mono-carbene species upon dissolution in deuterated solvent (see Figures 31S and 32S in Supporting Information).

The Au(I) and Au(III) complexes herein obtained were tested as catalyst for a benchmark organic reaction such as the cyclization of the propargylic amides, while the co-presence of both bis-carbene and mono-carbene species, as well as multiple counterions for $2_{\text{bis-I}_3/\text{AuI}_4}$, led us to exclude these latter iodine oxidation products as possible catalysts.

Structural Analysis

Solid state molecular structures

Crystals of complexes 1-Cl_3 , $1_{\text{bis-AuBr}_2}$ and 1-Br_3 , were obtained by dissolving the corresponding microcrystalline powders in the smallest volume of acetonitrile and by layering with diethyl ether. The solid-state molecular structures of 1-Cl_3 , $1_{\text{bis-AuBr}_2}$ and 1-Br_3 are depicted in Figure 1. As expected, complexes 1-Cl_3 and 1-Br_3 have a four-coordinated gold atom in a square-planar environment. The Cl(1)–Au(1)–Cl(3) and Br(2)–Au(1)–Br(3) bonds are nearly linear, with angles of 175.94(4) and 175.72(5)° while the C(1)–Au(1) distances is, respectively, 1.994(4) Å (1-Cl_3) and 1.978(11) Å (1-Br_3), which is in accordance with published NHC–Au(III) trichloride^[20,22b-c] and tribromide^[23,29] complexes. Finally, the Au–Cl_{trans} (2.3265(11) Å) and Au–Br_{trans} (2.4445(13) Å) distances were found to be slightly longer than the other Au–Cl and Au–Br bonds (Figure

1). $1_{\text{bis-AuBr}_2}$ was found to be a bis-carbene species instead of the expected NHC–AuBr. The theoretical formation of molecular structures similar to the one of $1_{\text{bis-Br}}$ was rationalized by Gust *et al.*^[30] according to a ligand scrambling mechanism between two paired mono-carbene-gold(I)bromide moieties by closed shell d¹⁰–d¹⁰ interactions. A rather similar molecular structure has been reported for an iodine ($1_{\text{bis-I}}$) analogue in the literature.^[31]



Figure 1. ORTEP plots of 1-Cl_3 , 1-Br_3 and $1_{\text{bis-AuBr}_2}$. Selected bond lengths (Å) and angles (deg) for 1-Cl_3 : Au1–C1 1.994(4), Au1–Cl2 2.3265(11), C1–Au1–C12 180.0, Cl1–Au1–Cl3 175.94(4); for 1-Br_3 : Au1–C1 1.978(11), Au1–Br1 2.4445(13), C1–Au1–Br1 180.0, Br2–Au1–Br3 175.72(5) and for $1_{\text{bis-AuBr}_2}$ Au1–C1 2.035(9), Au1–C10 2.035(9), C1–Au1–C1* 180.0.

Crystals of 2-Cl_3 , 2-Br_3 (Figure 2), 2-Br and $2_{\text{bis-I}}$ (Figure 3) were obtained by dissolving the crude products in dichloromethane and by layering hexane. Two crystallographic independent and chemically identical molecules were observed in both structures of complexes 2-Cl_3 and 2-Br_3 . As before, in both complexes the gold center exhibits a well-defined square-planar geometry and the Cl(2)–Au(1)–Cl(3) (177.26(6)°) and Br(2)–Au(1)–Br(3) (175.72(5)°) bonds were almost linear. Finally, the C(1)–Au(1) distances are 1.994(4) Å (2-Cl_3) and 1.978(11) Å (2-Br_3) (Fig. 2).

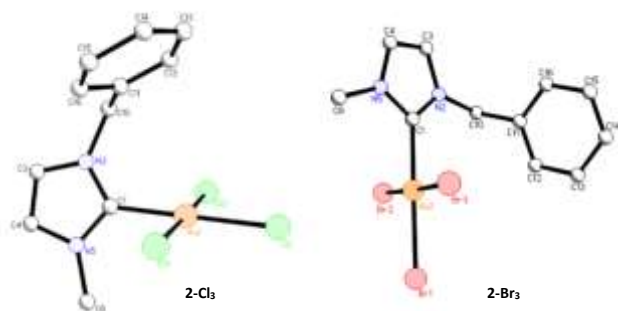


Figure 2. ORTEP plots of **2-Cl₃**, **2-Br₃**. Selected bond lengths (Å) and angles (deg) for **2-Cl₃**: Au1–C1 1.994(4), Au1–Cl1 2.3265(11), C1–Au1–C11 180.0, Cl2–Au1–Cl3 177.26(6) and for **2-Br₃**: Au1–C1 1.978(11), Au1–Br1 2.4445(13), C1–Au1–Br1 180.0, Br2–Au1–Br3 175.72(5).

In contrast to **1_{bis}-AuBr₂**, complex **2-Br** was obtained as a mono-carbene species while, conversely, in the **2_{bis}-I** complex the bis-carbene moiety and the AuI₂⁻ counterion were formed. For **2_{bis}-I**, both cation and anion are on special position with 2/m symmetry (C2h) (Figure 3) leading to some disorder in the phenyl rings, resulting in a reduced symmetry.

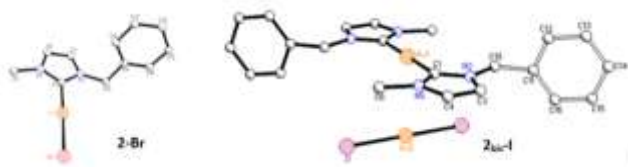


Figure 3. ORTEP plots of **2-Br**, **2_{bis}-I**. Selected bond lengths (Å) and angles (deg) for **2-Br**: Au1–C1 1.980(6), Au1–Br1 2.3902(8), C1–Au1–Br1 176.57(16) and for **2_{bis}-I**: Au1–C1 2.038(7), C1–Au1–C1* 180.0.

The crystal structures of **1_{mono}-I₃** and **1_{bis}-AuI₂** have been already discussed in the literature^[27] while those of **2_{mono}-I₃** and **2_{bis}-I₃/AuI₄** are here reported (Figure 4). Some crystallographic details, such as the Au–C_{carbene} and Au–X bond lengths and C_{carbene}–Au–X or X_{cis}–Au–X_{trans} bond angles for the molecular structures in this work, are reported in Tables 2 and 3. For completeness of the information, additional bond lengths and angles were taken from the literature.^[15,27,31] The analysis of the data highlights some striking features, for example: for the Au–C_{carbene} bond, longer bond lengths are observed for the bis-carbene compared to the mono-carbene species. Additionally, despite the increase of the oxidation state at the gold center, the Au–X_{trans} bond length, representing the bond in trans to the carbene carbon, is shorter in gold(I) than in gold(III) complexes. The gold oxidation state influences also the Au–X_{cis} bond lengths, where X_{cis} is in the halide in cis position with respect to the carbene; these bond lengths are shorter than those observed in Au–X_{trans} and in the corresponding gold(I) compounds, as evidenced in Table 2 for **1-Cl** and **1-Cl₃**, **2-Cl** and **2-Cl₃**, and **2-Br** and **2-Br₃**. As depicted in Table 3, the square planar

geometry of the Au–X₃ complexes appears notably regular, resulting in a subtle compression of the C_{carbene}–Au–X_{cis} bond angles from 90°, and a concurrent expansion of the X_{cis}–Au–X_{trans} bond angles.

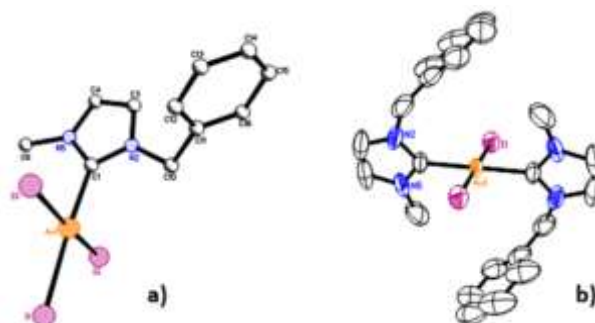


Figure 4. ORTEP plots of **2_{mono}-I₃** a) and **2_{bis}-I₃/AuI₄** cationic moiety b). Selected bond lengths (Å) and angles (deg) for **2_{mono}-I₃**: Au1–C1 2.033(11), Au1–I3 2.6110(10), Au1–I2 2.6151(9), Au1–I1 2.6179(9) C1–Au1–I1 176.1(3) and for **2_{bis}-I₃/AuI₄** (anions are omitted): Au1–C1 2.037(7), Au1–I1 2.6290(6) Au1–C1 2.038(7), C1–Au1–C1* 180.

Table 2. Selected Au–C_{carbene} and Au–X Bond Distances (Å) for all the gold(I) and gold(III) complexes. For completeness, some data were collected from the literature reported in the square brackets.

Complex	C _{carb} -Au-X _{trans}	C _{carb} -Au-C _{carb}	C _{carb} -Au-X _{cis1}	C _{carb} -Au-X _{cis2}	X _{trans} -Au-X _{cis1}	X _{cis1} -Au-X _{cis2}
1-Cl ^[15]	178.9(6)	-	-	-	-	-
1-Cl₃	180.0	-	87.97(2)	87.97(2)	92.03(2)	92.03(2)
2-Cl	176.9(2)	-	-	-	-	-
2-Cl₃ ^a	179.69(18)	-	88.12(17)	88.67(17)	92.08(6)	91.14(7)
1_{bis}-AuBr₂		180.0	-	-	-	-
1-Br₃ ^a	180.0	-	87.86(2)	87.86(2)	92.14(2)	92.14(2)
2-Br	176.57(16)	-	-	-	-	-
2-Br₃	179.4(3)	-	89.2(2)	88.6(2)	91.27(4)	90.91(4)
1_{bis}-I ^[31]		178.80	-	-	-	-
1_{mono}-I₃ ^[27]	180.0	-	87.31	87.31	92.69	92.69
1_{bis}-AuI₂ ^[27]	-	180.0	90.45 (C ₁ -Au-X _{cis1})	89.55 (C ₁ -Au-X _{cis2})	-	-
2_{bis}-I	180.0	-	-	-	-	-
2_{mono}-I₃	176.1(3)	-	87.6(3)	87.8(3)	91.81(3)	93.08(3)
2_{bis}-AuI₄/I₃	-	180.0	88.4(2) (C ₁ -Au-X _{cis1})	91.6(2) (C ₁ -Au-X _{cis2})	-	-

^a Data are reported for one of the two independent crystallographic units. ^b Au-X_{cis1} and Au-X_{cis2} are the halides in cis to the gold-C_{carbene} bond.

Table 3. Selected bond angle values of C_{carbene}-Au-X (° deg) for all the gold(I) and gold(III) complexes. For completeness, some data were collected from the literature reported in the round brackets.

Complex	Au-C _{carbene}	Au-X _{trans}	Au-X _{cis1} ^b	Au-X _{cis2} ^b
1-Cl ^[15]	1.95(2)	2.302(4)	-	-
1-Cl₃	1.994(4)	2.3265(11)	2.2732(9)	2.2732(9)
2-Cl	1.990(8)	2.269(2)	-	-
2-Cl₃ ^a	1.988(5)	2.3084(16)	2.2676(17)	2.2739(16)
1_{bis}-AuBr₂	2.035(9) (Au-C ₁); 2.035(9) (Au-C ₂)	-	-	-
1-Br₃ ^a	1.978(11)	2.4445(13)	2.4282(10)	2.4283(10)
2-Br	1.980(6)	2.3902(8)		
2-Br₃	2.007(8)	2.4495(10)	2.4165(11)	2.4171(10)
1_{bis}-I ^[31]	2.028 (Au-C ₁); 1.988 (Au-C ₂)	-	-	-
1_{mono}-I₃ ^[27]	2.074	2.623	2.626	2.626
1_{bis}-AuI₂ ^[27]	2.021(7) (Au-C ₁); 2.021(7) (Au-C ₂)	-	2.621	2.621
2_{bis}-I	2.038(7) (Au-C ₁); 2.038(7) (Au-C ₂)	-	-	-
2_{mono}-I₃	2.033(11)	2.6179(9)	2.6110(10)	2.6151(9)
2_{bis}-AuI₄/I₃	2.037(7) (Au-C ₁); 2.037(7) (Au-C ₂)	-	2.6290(6)	2.6290(6)

Catalytic Studies

The gold(I/III)-catalyzed oxazole synthesis^[32] was chosen as benchmark reaction for the assessment of the catalytic activity of the gold(I) and gold(III) complexes prepared herein. In a study published in 2010 by Hashmi *et al.*^[13], the conversion of propargylic amide was found to be influenced by the oxidation state of the gold catalysts (Scheme 2), demonstrating that oxazole **B** (Au(III) catalysis) or methylenedihydrooxazole **A** (Au(I) catalysis) could be obtained with high chemoselectivity. Thus, in this work, the 4-methoxy-N-(2-propyn-1-yl)benzamide and the 4-methoxy-N-(3-phenylprop-2-ynyl)benzamide were prepared according to published procedures^[33] and applied as test model. Initially, all the reactions were conducted at room temperature in NMR tubes in d³-acetonitrile. 4-methoxy-N-(2-propyn-1-yl)benzamide (25 mg, 0.13 mmol) was dissolved in CD₃CN (200 μL). The solution was then transferred into a 5 mm NMR tube and charged with 1 mol% the gold(I/III)-catalyst, without addition of silver salts, and the mixture was vigorously shaken. The time count was started simultaneously. The progress of the reaction was monitored by ¹H NMR at 25 °C.^[4] As expected, all the NHC-gold(I) complexes (**1-Cl**, **1_{bis}-AuBr₂**, **1_{bis}-I**, **2-Cl**, **2-Br** and **2_{bis}-I**) and almost all the NHC-gold(III) (namely, **1-Cl₃**, **1-Br₃** and **2-Br₃**) were found inactive toward this reaction and no conversion was detected after 24 hours. Noteworthy, an activity was revealed for 1-benzyl-3-methyl-NHC-AuCl₃ (**2-Cl₃**) after 24 hours and a quantitative conversion of the propargylamide to the aromatic oxazole **C** was observed within 7 days. Interestingly, by monitoring the reaction by ¹H NMR over time, the formation of the intermediate dihydrooxazole **B-1** (Figure 5) was observed during the first two days of reaction after the protodeauration step^[13] that finally aromatized to **C**. The detection of **B-1** as an intermediate for the formation of **C** was meaningful to propose a mechanism where the gold(I/III), acting as Lewis acids on the regard of the alkynyl moiety, activates the intramolecular rearrangement resulting to **B** converting to **B-1** by a protodeauration. Finally, **B-1** converges to the aromatic **C**, as reported in Scheme 6. More grateful outcomes were obtained in the presence of 1 mol% AgPF₆ and the catalytic activity of almost every complex was boosted (Table 4).

Table 4: Reactions were carried out at room temperature in CD₃CN. Conversion was determined by NMR spectroscopic measurements.

#	Catalyst	Time, ^a T	Conversion(%)	
			B	C
1	1-Cl	7d, RT	77	3
2	1-Cl₃	72h, RT	traces	> 99
3	1_{bis}-AuBr₂	7d, RT	20	traces
4	1-Br₃	7d, RT	40	traces
5	1_{bis}-I	7d, RT	0	0
6	2-Cl	7d, RT	85	8
7	2-Cl₃	7d, RT	0	18
8	2-Br	7d, RT	69	1
9	2-Br₃	7d, RT	0	0
10	2_{bis}-I	7d, RT	46	1

Interestingly, the same reactions in the presence of **2-Cl** and **2-Cl₃** (1% mol, with or without the silver salt) were conducted with 4-methoxy-N-(3-phenylprop-2-ynyl)benzamide but no conversions were observed neither to the oxazole nor to the dihydrooxazole (see Supporting Information Figures 47S-50S).

The results are summarized in Table 4. In the last two columns on the right of table the conversion percent are reported; they are largely variable indicating an extent of chemoselectivity among the gold(I) and the gold(III) complexes. In the context of the 1,3-dimethyl-NHC-gold(I/III) series, complex **1-Cl₃** exhibited complete conversion to **C** after 72 hours (entry 2). Conversely, complex **1-Br₃** (entry 4) only resulted in the formation of **B**, with the aromatic oxazole **C** appearing only in traces. Moving to the 1,3-dimethyl-NHC-gold(I) congeners, a gradual increase in conversion was observed from **1_{bis}-I** (entry 5, no conversion) to **1_{bis}-AuBr₂** (entry 3, 20% conversion) culminating in **1-Cl** (entry 1) with a substantial 77% conversion to **B**.

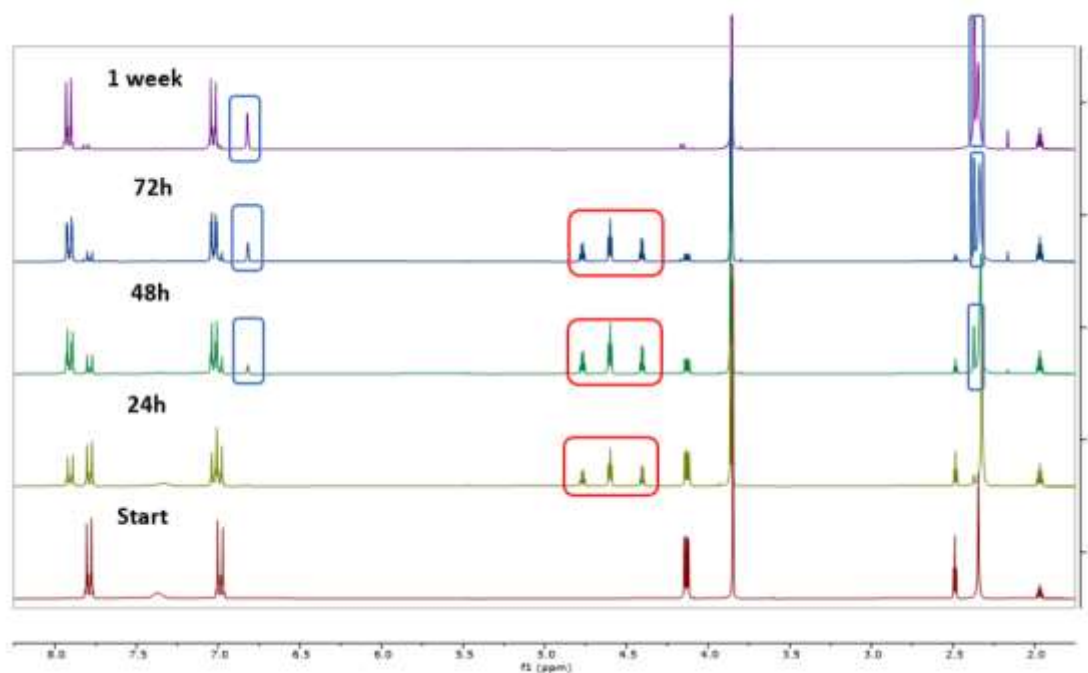
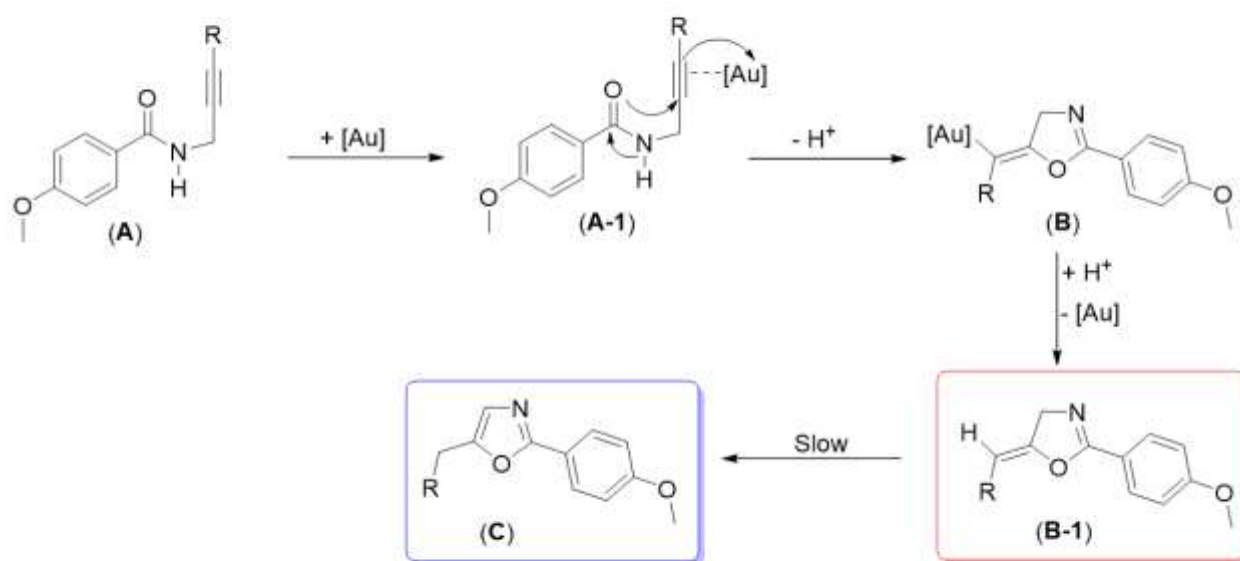


Figure 5. Superimposed ^1H NMR spectra for the cycloisomerization catalyzed by **2-Cl₃**.



Scheme 6. Mechanism for the cycloisomerization of **A** to **C** ($\text{R} = \text{H}$, if $\text{R} = \text{Ph}$ no conversion is observed).

Surprisingly, even complex **1-Cl**, previously believed to cleanly halt at intermediate **B**, displayed an unexpected 3% conversion to **C**. This outcome is noteworthy as there is no existing literature evidence for aromatic oxazoles produced by gold(I) catalysts. Regarding the 1-benzyl-3-methyl-NHC-gold(I/III) series, compound **2-Cl** (entry 6) exhibited a similar behaviour to **1-Cl**, with nearly identical conversion to **B**. However, the conversion to the aromatic oxazole **C** increased to 8% when **2-Cl** was employed with respect

to **1-Cl** (entry 1, 3% conversion to **C**), putting some hints about the metal oxidation state's lack of influence. Notably, a higher conversion to **B** was observed for **2-Br** (entry 8, 69% conversion) compared to **1_{bis}-AuBr₂** (entry 3, 20% conversion), suggesting that the presence of the benzyl group enhances the catalytic activity of the catalyst. Finally, **2-Cl₃** was found to be negatively influenced by the presence of silver salt AgPF_6 as the conversion to the aromatic oxazole **C** decreased to 20% in a week (entry

7) compared to using **2-Cl₃** alone in which a quantitative conversion was reached in the same amount of time. Additionally, during the monitoring of the reaction catalysed by **2-Cl₃/AgPF₆**, the formation of intermediate **B** was not observed as previously seen when **2-Cl₃** was employed alone (see Figure 5), thus suggesting the possible presence of a catalytic cycle that does not proceed through the formation of the non-aromatic intermediate **B**.

Conclusions

In this work, a series of NHC-Au(I) and the corresponding NHC-Au(III) complexes obtained by halogen addition reactions have been synthesized and structurally characterized. Selected gold(I) and gold(III) complexes belonging to this series of compounds have been tested as catalysts for the cycloisomerization of a propargylamide as benchmark reaction. Contrary to the findings reported in existing literature in which Au(III) complexes were the only catalysts promoting the chemoselective cycloisomerization of 4-methoxy-N-(2-propyn-1-yl)benzamide towards oxazoles,^[13] this study revealed that selected NHC-Au(I) complexes can also induce the predominant formation of aromatic oxazole with respect to the intermediate methylenedihydrooxazole. The reaction conditions involved a 1 mol% catalyst load, with the addition of silver salts. Noteworthy within this series, one Au(III) carbene complex, the 1-benzyl-3-methyl-imidazolyl-2-yl-Au-Cl₃, was able to promote the conversion to the oxazole even in absence of silver salt. The relatively sluggish kinetics of the cycloisomerization were monitored by ¹H NMR over the course of a week, confirming a 5-*exo*-dig cyclization in the catalytic cycle that can result in the formation of the aromatic oxazole after isomerization. Finally, the methylenedihydrooxazole and the aromatic oxazole were achieved in different ratios when employing gold catalysts in both possible oxidation states. This observation releases any potential involvement of the oxidation state in the catalyst activity, as previously suggested in the literature.^[29] Conversely, the distinct halide and the presence of halide scavengers were found to significantly influence the chemoselectivity, with the steric hindrance of the NHC ligand in the gold complexes exerting only a modest impact.

Experimental Section

General information

Chemicals were bought from commercial suppliers (abcr, Acros, Alfa Aesar, BLDPharm, Carbolution, Chempur, Fluka, Merck, Sigma Aldrich and TCI) and

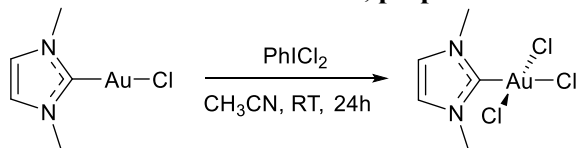
used as delivered. Anhydrous solvents were dispensed from a solvent purification system MB SPS-800. Solvents were degassed by freeze-pump-thaw technique. Deuterated solvents were bought from Eurisotop and Sigma Aldrich. Compound **1-Cl** was synthesized according to a procedure published in the literature by some of us.^[12] The synthesis of **2-Cl** followed the same procedure but employing chloro(dimethylsulfide)gold(I) instead of chloro(tetrahydrothiophene)gold(I).

Nuclear magnetic resonance (NMR) spectra were recorded at room temperature on an Oxford-400 Varian spectrometer (400.4 MHz for ¹H and 100 MHz for ¹³C) at the Chemistry Interdisciplinary Project (ChIP) in Camerino or at the organic chemistry department of Heidelberg University under the supervision of Dr. J. Graf on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Fourier 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz), Bruker Avance NEO 700 (700 MHz). Chemical shifts δ are given in ppm and coupling constants J in Hz. Spectra were referenced to residual solvent protons according to Fulmer et al.^[34] or for TCE-d₂ to 6.00 ppm (¹H) and 73.8 ppm (¹³C) respectively. The following abbreviations were used to describe the observed multiplicities: for ¹H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sext = sextet, sept = septet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad signal; for ¹³C{¹H} NMR spectra: s = quaternary carbon, d = CH carbon, t = CH₂ carbon and q = CH₃ carbon. ¹³C{¹H} NMR spectra are proton decoupled and interpreted with help of DEPT- and 2D spectra. All spectra were integrated and processed using MestreNova software.

Infrared spectra were recorded from 4000 to 600 cm⁻¹ with a Perkin-Elmer SPECTRUM ONE System FT-IR instrument or on a FT-IR spectrometer (Bruker LUMOS) with a Germanium ATR-crystal from a neat powder or oil. For the most significant bands the wave numbers are given. IR annotations used: br = broad, m = medium, s = strong, sh = shoulder, vs = very strong, w = weak and vw = very weak.

Elemental analyses (C, H, N, S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument.

X-ray crystallography was carried out at the chemistry department of Heidelberg University under the supervision of Dr. F. Rominger on the following instruments: Bruker Smart APEX II Quazar (with Momicrosource) and Stoe Stradivari (with Comicrosource and Pilatus detector). The structures were processed with Mercury 4.3.0.

Preparation of the compounds**Reaction of 1-Cl with PhICl₂, preparation of 1-Cl₃**

1,3-dimethyl-imidazol-2-yl-gold(I) chloride (100mg, 0.304mmol) was dissolved in 10mL of acetonitrile, then solid iodobenzene dichloride (125,51mg, 0.457mmol) was added. The reaction was stirred for 24h at room temperature under nitrogen atmosphere. After 24 hours, the yellow solution was evaporated under reduced pressure and the resulting yellow solid was washed with n-hexane (2x5mL) and dried under vacuum. Finally, slow diffusion of diethyl ether into an acetonitrile solution of the crude product gave colorless crystals of **1-Cl₃** that were filtered and dried under vacuum. Yield: 98%.

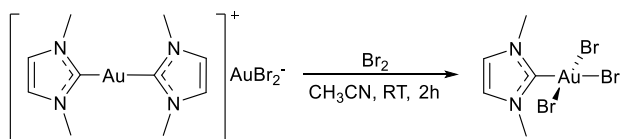
¹H NMR (δ, room temperature, CD₃CN): 7.25(s, 2H), 3.81(s, 3H).

¹³C NMR (δ, room temperature, CD₃CN): 147.00, 125.01, 36.97.

IR (cm⁻¹): 3308, 3157, 3122, 2956, 1721, 1697, 1624, 1585, 1574, 1498, 1436, 1411, 1339, 1303, 1279, 1230, 1146, 1084, 1044, 846, 765, 738, 669, 622, 614.

Elemental Analysis for C₅H₈N₂AuCl₃ calcd %: C 15.03; H 2.02; N 7.01; found %: C 14.73; H 2.05; N 6.97.

Elemental Analysis for C₁₀H₁₆N₄Au₂Br₂ calcd %: C 16.10; H 2.16; N 7.51; found %: C 16.29; H 2.22; N 7.62.

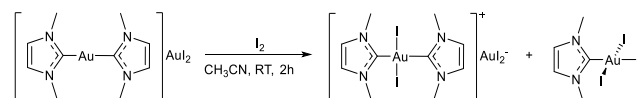
Reaction of 1_{bis}-AuBr₂ with bromine, preparation of 1-Br₃

[bis-(1,3-dimethyl-imidazol-2-yl)]gold(I) dibromoaurate (50mg, 0.77mmol) was dissolved in 10mL of acetonitrile, then liquid bromine (36,48mg, 11μL, 0,227mmol) were added. The reaction was stirred for 2h at room temperature under nitrogen atmosphere. The solution was evaporated under reduced pressure and the resulting dark orange solid was washed with n-hexane (2x5mL) and dried under vacuum. Finally, slow diffusion of diethyl ether into an acetonitrile solution of the crude product gave orange crystals of **1-Br₃** that were filtered and dried under vacuum. Yield = 93%

¹H NMR (δ, room temperature, CD₃CN): 7.35(s, 2H), 3.85(s, 3H).

¹³C NMR (δ, room temperature, CD₃CN): 136.60, 125.40, 37.43.

IR (cm⁻¹): 3154, 3121, 2927, 1729, 1700, 1628, 1603, 1572, 1493, 1440, 1411, 1341, 1231, 1086, 754, 740, 686, 666, 615.

Reaction of 1_{bis}-I with iodine, preparation of 1_{mono}-I₃ and 1_{bis}-AuI₂

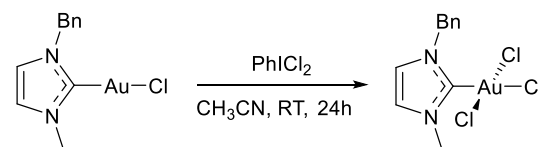
[bis-(1,3-dimethyl-imidazol-2-yl)]gold(I) diiodoaurate (50mg, 0.59mmol) was dissolved in 10mL of acetonitrile, under nitrogen atmosphere, and then solid iodine (45.32mg, 0.178mmol) was added. The reaction was stirred for 2h at room temperature under nitrogen atmosphere. After 2 hours, the red solution was evaporated under reduced pressure, and the resulting reddish solid was washed with n-hexane (2x10 mL) and dried under vacuum. Finally, slow diffusion of diethyl ether into an acetonitrile solution of the crude product gave dark two types of red crystals that were filtered and dried under vacuum resulting in crystals of **1_{mono}-I₃** and of **1_{bis}-AuI₂** Yield = 76%.

¹H NMR (δ, room temperature, CD₃CN): 7.39 (s, 4H, **1_{bis}-AuI₂**), 7.34 (s, 2H, **1_{mono}-I₃**), 3.80 (s, 12H, **1_{bis}-AuI₂**), 3.74 (s, 6H, **1_{mono}-I₃**)

¹³C NMR (δ, room temperature, CD₃CN): 125.63, 125.40, 37.41, 37.58.

IR (cm⁻¹): 3121, 2940, 1679, 1588, 1565, 1504, 1487, 1456, 1428, 1400, 1335, 1227, 1143, 1082, 840, 741, 684, 661, 637, 617.

Elemental Analysis for 6C₅H₈N₂AuI₃ : 1C₁₀H₁₆N₂Au₂I₄ calcd %: C 9.35; H 1.26; N 4.36; found %: C 9.37; H 1.15; N 4.28.

Reaction of 2-Cl with PhICl₂, preparation of 2-Cl₃

1-benzyl-3-methyl-imidazol-2-yl-gold(I) chloride (50mg, 0.123mmol) was dissolved in 10mL of acetonitrile, then solid iodobenzene dichloride (50,95mg, 0.185mmol) was added. The reaction was stirred for 24h at room temperature under nitrogen atmosphere. The yellow solution was evaporated under reduced pressure, and the resulting yellow solid was washed with n-hexane (2x5mL) and dried under

vacuum. Finally, slow diffusion of n-hexane into a dichloromethane solution of the crude product gave yellow crystals of **2-Cl₃** that were filtered and dried under vacuum. Yield = 88%

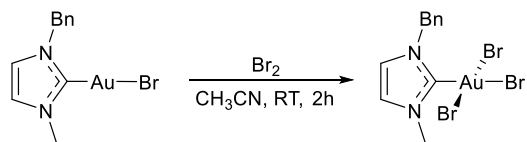
¹H NMR (δ, room temperature, CD₃CN): 7.44-42 (m, 5H), 7.39 (d, J = 2.1 Hz, 1H), 7.35 (d, J = 2.1 Hz, 1H), 5.48 (s, 2H), 3.93 (s, 3H).

¹³C NMR (δ, room temperature, CD₃CN): 138.97, 134.94, 129.63, 129.46, 129.25, 126.28, 124.81, 54.51, 38.14.

IR (cm⁻¹): 3154, 3122, 1568, 1489, 1455, 1406, 1363, 1329, 1240, 1208, 1154, 1080, 786, 760, 732, 706, 696, 680, 645.

Elemental Analysis for C₁₁H₁₂N₂AuCl₃ calcd %: C 27.78; H 2.54; N 5.89; found %: C 27.58; H 2.73; N 6.06.

Reaction of **2-Br** with bromine, preparation of **2-Br₃**



1-benzyl-3-methyl-imidazol-2-yl-gold(I) chloride (50mg, 0.123mmol) was dissolved in 10mL of acetonitrile, then liquid bromine (50.95mg, 9μL, 0.185mmol) was added. The reaction was stirred for 2h at room temperature under nitrogen atmosphere. The dark orange solution was then evaporated under reduced pressure, and the resulting solid was washed with n-hexane (2x5mL) and dried under vacuum. Finally, slow diffusion of n-hexane into a dichloromethane solution of the crude product gave yellow crystals of **2-Br₃** that were filtered and dried under vacuum. Yield = 84%

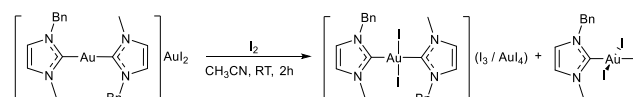
¹H NMR (δ, room temperature, CD₃CN): 7.43 (m, 5H), 7.38 (d, J = 2.2 Hz, 1H), 7.31 (d, J = 2.2 Hz, 1H), 5.43 (s, 2H), 3.87 (s, 3H).

¹³C NMR (δ, room temperature, CD₃CN): 136.70, 133.79, 128.73, 128.63, 128.59, 125.43, 123.83, 53.77, 37.45.

IR (cm⁻¹): 3151, 3119, 3027, 2952, 1588, 1567, 1484, 1455, 1403, 1362, 1329, 1239, 1206, 1188, 1158, 1128, 1078, 1030, 1001, 955, 920, 846, 785, 751, 729, 703, 695, 677, 644.

Elemental Analysis for C₁₁H₁₂N₂AuBr₃ calcd %: C 21.70; H 1.99; N 4.60; found %: C 21.70; H 2.10; N 4.62.

Reaction of **2_{bis}-I** with iodine, preparation of **2_{mono}-I₃** and **2_{bis}-I₃/AuI₄**



[(bis-1-benzyl-3-methyl-imidazol-2-yl)]gold(I) diiodoaurate (125mg, 0.126mmol) was dissolved in 10mL of acetonitrile, then solid iodine (95.63mg, 0.378mmol) was added. The reaction was stirred for 2h at room temperature under nitrogen atmosphere. After 2 hours, the red solution was evaporated under reduced pressure, and the resulting reddish solid was washed with n-hexane (2x10 mL) and dried under vacuum. Finally, slow diffusion of n-hexane into a dichloromethane solution of the crude product gave brown crystals of three different type affording to different gold(III) compounds as **2_{mono}-I₃** and **2_{bis}-I₃/AuI₄** that were filtered and dried under vacuum. Yield = 70%

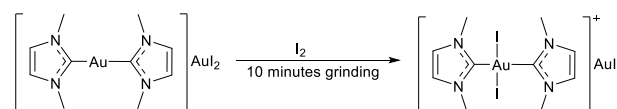
¹H NMR (δ, room temperature, CD₃CN): 7.46-7.40 (m), 7.37-7.36 (d), 7.26(d) 5.40 (s, 4H), 5.34 (s, 2H), 5.24 (s, 4H), 3.84 (s, 6H), 3.76 (s, 3H), 3.70 (s, 6H).

¹³C NMR (δ, room temperature, CD₃CN): 144.97, 137.43, 134.65, 134.40, 129.82, 129.64, 129.59, 129.58, 129.46, 129.37, 129.34, 129.10, 129.03, 126.71, 126.55, 126.27, 125.34, 125.16, 124.71, 54.87, 54.79, 54.68, 38.86, 38.76, 38.48.

IR (cm⁻¹): 3734, 3151, 3124, 3101, 3028, 2938, 1953, 1583, 1566, 1478, 1453, 1415, 1365, 1227, 1156, 1129, 1077, 1027, 963, 843, 777, 743, 730, 697, 656, 613.

Elemental Analysis for 4C₁₁H₁₂N₂AuI₃: 1C₂₂H₂₄N₄AuI₅: 1C₂₂H₂₄N₄Au₂I₆ calcd %: C 18.62; H 1.71; N 3.95; found %: C 18.60; H 1.84; N 3.93.

Solventless mechanochemical reaction of **1_{bis}-I** with iodine



Solid **1_{bis}-I** (40 mg; 0.048 mmol) was mixed in a mortar with solid iodine (18 mg; 0.071 mmol) for 10 minutes with few drops of CH₃CN. The resulting solid was dissolved with CH₃CN, filtered through celite, and dried at reduced pressure. The solid was then washed with hexane (2 × 5 mL) to remove the excess of iodine. Yield = 85%.

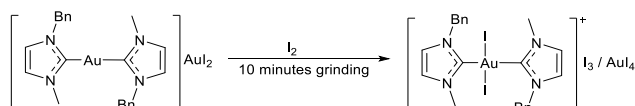
¹H NMR (δ, room temperature, CD₃CN): 7.40 (s, 4H), 3.81 (s, 12H)

¹³C NMR (δ, room temperature, CD₃CN): 144.43, 125.62, 37.61

MIR (cm⁻¹): 3148(w), 3097(w), 2939(w), 1565(w), 1482(m), 1433(w), 1397(w), 1338(w), 1227(m), 1079(m), 740(s), 683(s).

FIR (cm⁻¹): 682(s), 662(w), 613(w), 565(w), 540(w), 488(w), 453(m), 394(w), 342(m), 295(w), 203(m), 187(w), 163(m), 136(m), 106(m).

Solventless mechanochemical reaction of **2**_{bis}-**I** with iodine



Solid **2**_{bis}-**I** (30 mg; 0.030 mmol) was mixed in a mortar with solid iodine (12.6 mg; 0.045 mmol) for 10 minutes with few drops of CH₃CN. The resulting solid was dissolved with CH₃CN, filtered through celite, and dried at reduced pressure. The solid was then washed with hexane (2 × 5 mL) to remove the excess of iodine. Yield = 90%

¹H NMR (δ, room temperature, CD₃CN): 7.43-7.26 (m), 5.41, 5.25, 3.85, 3.70.

¹³C NMR (δ, room temperature, CD₃CN): 144.50, 134.17, 129.10, 129.05, 128.84, 128.55, 126.18, 124.82, 124.65, 54.35, 38.28.

MIR (cm⁻¹): 3151(w), 3118(w), 3097(w), 1565(w), 1478(m), 1451(m), 1415(w), 1362(w), 1335(w), 1224(m), 1187(m), 1076(m), 1027(m), 997(w), 958(w), 731(vs), 686(vs), 451(m).

FIR (cm⁻¹): 686(s), 609(w), 578(w), 466(w), 451(m), 354(w), 238(w), 200(m), 161(w), 136(s), 125(s), 106(s).

Crystallographic Data

CCDC-2360511 (**1-Cl**₃), -2360512 (**1**_{bis}-**AuBr**₂), -2360513 (**1-Br**₃), -2360514 (**2-Cl**), -2360515 (**2-Cl**₃), -2360516 (**2-Br**), -2360517 (**2-Br**₃), -2360518 (**2**_{bis}-**I**), -2360519 (**2**_{bis}-**AuI**₂) and -2360520 (**2**_{bis}-**I**₃) contain 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/structures

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Research Article

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Nicola Sargentoni, Rossana Galassi,* Lorenzo Luciani, Frank Rominger, Matthias Rudolph, A. Stephen K. Hashmi*

