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Mono- and Digold(I) Complexes with Mesoionic Carbenes: Structural Characterization and Use in Catalytic Silver-Free Oxazoline Formation

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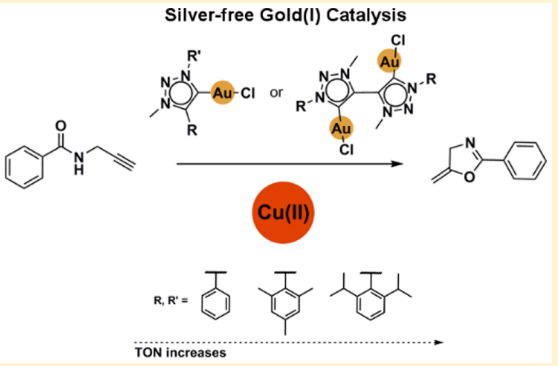
Supporting Information

ABSTRACT: Triazolylidenes are a prominent class of mesoionic carbenes that have found use as supporting ligands in homogeneous catalysis in recent years. We present here the syntheses of three new mononuclear gold(I) chlorido and two new dinuclear gold(I) chlorido complexes. The ligands in the aforementioned complexes are derived from either the corresponding monotriazolium or the bitriazolium salts. All complexes have been characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction studies. Structural characterization delivers a delocalized bonding situation within the triazolylidene ligands and a linear coordination at the gold(I) centers. The gold(I) centers in all cases are bound to one triazolylidene-*C* donor and a chlorido ligand. Additionally, for the digold(I) complexes large Au−Au distances were observed, ruling out the existence of aurophilic interactions in these digold complexes in the solid state. All of the gold(I) complexes were tested as (pre)catalysts for the cyclization reaction of propargylic amides to form oxazolines. We show here that the steric bulk of the substituents on the triazolylidene ligands plays a decisive role in the catalytic efficiency of the gold(I) complexes. Copper(II) triflate is shown as a viable alternative to silver(I) salts as an additive for the oxazoline formation. Mechanistic studies show the detection of a gold(I) triazolylidene vinyl complex as an intermediate in the catalytic synthesis of oxazoline with these complexes. These results thus establish copper(II) triflate as an alternative to silver(I) salts as an additive in gold(I) triazolylidene catalysis. Furthermore, it also shows that steric tuning of triazolylidene ligands can indeed be utilized for increasing the catalytic efficiency of the corresponding complexes.



INTRODUCTION

1,2,3-Triazol-5-ylidenes belong to the class of so-called mesoionic carbenes (MICs).[1] The easy access to these classes of ligands through the copper(I) catalyzed azide−alkyne cycloaddition[2] and subsequent alkylation reactions have made them extremely popular in current chemistry. Since their first use as ligands in 2008[3] and their isolation in their free form in 2010,[4] these classes of MICs have found use as ligands in a host of metal-catalyzed homogeneous catalytic reactions.[1,5] Furthermore, their metal complexes have also been used for photochemical application,[6] and for investigations of redox properties.[7]

Even though many transition-metal complexes have been synthesized with these MIC ligands, late transition metals such as copper(I),[5e,8] ruthenium(II),[3,9] palladium(II),[3,10] iridium(III),[5b,c,9d−g,10k,11] and gold(I)[5f,12] have been often used in combination with these MIC ligands. For catalysis with gold(I) complexes, silver salts are traditionally used as activators.[13] However, recent years have seen the search for and emergence of other activators.[12g,h,14] Reasons for this search are sometimes based on cost considerations. Apart from that, the use of new activators can also lead to new kinds of catalytic reaction mechanisms or be helpful in cases where silver salts are "too aggressive" and lead to complex degradation.[12a] Furthermore, most copper(II) salts are far more moisture and light stable in comparison to silver(I) salts, thus making their handling easier. For gold(I), we recently presented examples of redox-active gold complexes with MIC ligands[15] and showed that redox-induced catalysis can be used for the synthesis of oxazolines. The oxidizing agent acetylferrocenium tetrafluoroborate alone (without the need for any additional activator) was enough to promote catalytic gold(I) triazolylidene induced oxazoline formation. In search of alternatives (both gold(I) complexes and activators) in the gold triazolylidene catalyzed oxazoline synthesis, we have now turned our attention to mono- and dinuclear gold(I) chlorido complexes (Scheme 1) with MIC ligands.

Below we present the synthesis and structural characterization of three mononuclear and two dinuclear gold(I) complexes. These complexes, together with a gold(I) complex known in the literature, were tested as precatalysts for the formation of oxazoline through the cyclization of propargylic amides. The influence of the substituents on the triazolylidene

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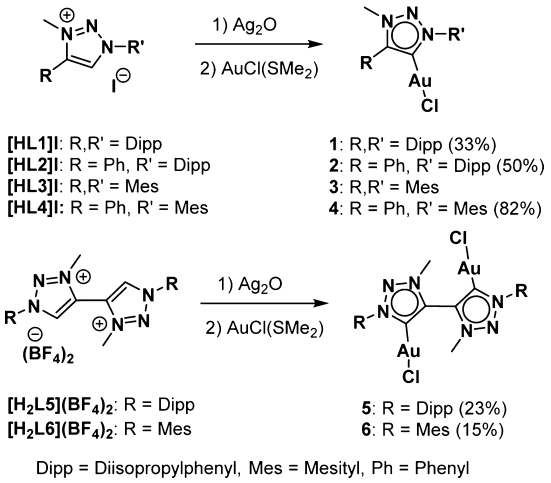
Scheme 1. Preparation of Mono- and Digold(I) MIC Complexes[a]



[a]Conditions: (1) KCl, Cs_2CO_3, CH_3CN, 3 days, room temperature; (2) CH_2Cl_2/ CH_3CN, 1 day, room temperature; Conditions for complex **4**: (1) CH_2Cl_2, overnight, room temperature; (2) CH_2Cl_2, 1 day, room temperature. Complex **3** was reported earlier and was resynthesized here for comparison purposes.[12a]

ligands on catalysis has been tested. Attempts have been made to characterize catalytic intermediates with the aim of understanding the reaction mechanism. Furthermore, we have also tested if copper(II) triflate can be used as an alternative additive to silver salts in gold(I) triazolylidene induced catalysis.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Gold(I) Complexes. The 1,2,3-triazolium salts used in this work were prepared according to procedures previously described in the literature.[4,5e,8f,g,10b] The 1,2,3-triazolium salt [**HL2**]**I** was synthesized by methylation of the corresponding 1,2,3-triazole **L2**[4] with iodomethane. In addition to four monotriazolium salts, two bitriazolium salts were synthesized as well (Scheme 1). The formation and purity of the salts were established by mass spectrometry and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. For the synthesis of the complexes, the 1,2,3-triazolium salts were first metalated with Ag_2O followed by transmetalation with $AuCl(SMe)_2$ to obtain the neutral gold(I) MIC complexes **1**, **2**, and **4**–**6** (Scheme 1). Complex **3** was already reported in 2013 and was used here only for comparison in the catalysis.[12a] All complexes were isolated as colorless solids. The yields of the mononuclear complexes **1**, **2**, and **4** (33–82%) were higher than those for the binuclear complexes **5** and **6** (15–30%), although KCl and Cs_2CO_3 were added to support the metalation as described previously by us.[15] For the synthesis of complex **4**, no additional salt and base were needed, presumably due to the less sterically demanding substituents on the triazolylidene ring. All gold(I) MIC complexes are air and moisture stable and are not light sensitive.

The formation of the gold(I) MIC complexes was established by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The first indication for this formation was the absence of the characteristic low-field triazolium proton signals in the ^{1}H NMR spectra. In agreement with previously reported complexes,[5f,12a] the carbene carbons in the ^{13}C{^{1}H} NMR spectra appear in the region δ 160–167 ppm. This is an unambiguous assignment for the existence of the complexes in solution. Additionally all complexes were characterized by ESI-MS methods (see the Experimental Section).

Single crystals of the 1,2,3-triazolium salt [**HL2**]**I** and the complexes **1**, **2**, **5**, and **6** were grown, and these crystals were analyzed by X-ray diffraction analysis.

Single crystals of [**HL2**]**I** were obtained by recrystallization from a mixture of dichloromethane and diethyl ether (2/1) at

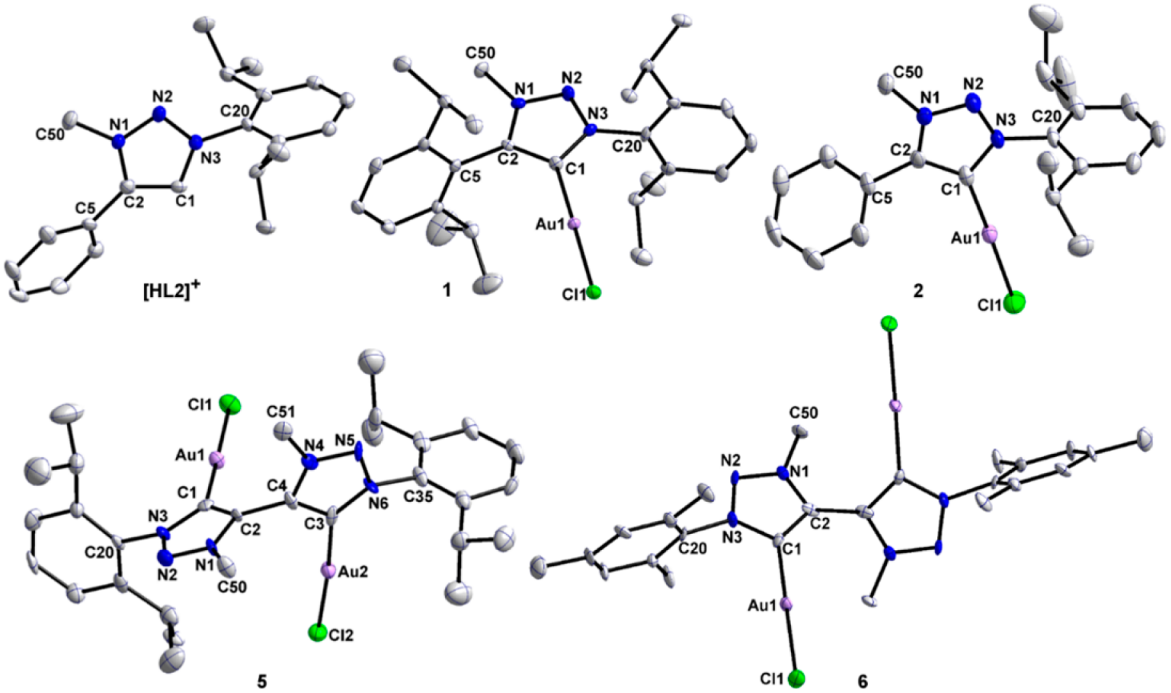


Figure 1. ORTEP diagrams of 1,2,3-triazolium salt [**HL2**]**I** (top left) and complexes **1** (top middle), **2** (top right), **5** (bottom left), and **6** (bottom right). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and anions have been omitted for clarity.

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Table 1. Selected Measured Bond Lengths (in Å) and Bond Angles (in deg) of Complexes 1, 2, 5, and 6

	1	2	5	6
C1−Au1−Cl1/C3−Au2−Cl2	178.5(2)	178.3(2)	177.6(3)/175.7(3)	177.2(3)
Au1−C1/Au2−C3	1.992(5)	1.968(5)	1.958(12)/1.981(12)	2.001(9)
Au1−Cl1/Au1−Cl2	2.295(2)	2.278(2)	2.284(3)/2.287(3)	2.276(2)

room temperature. The bond lengths and angles are similar to those observed in other 1,2,3-triazolium salts (Tables S3, S5, and S7 in the Supporting Information).[4,5e,8f,g,10b] Single crystals of the complexes **1**, **2**, and **6** were obtained by slow diffusion of hexane into a concentrated solution of dichloromethane at room temperature. Single crystals of the complex **5** were obtained by slow diffusion of diethyl ether into a concentrated solution in acetonitrile at room temperature. Crystallographic details for all compounds are given in Tables S1 and S2 in the Supporting Information.

As expected, the gold(I) centers are almost linearly coordinated in all complexes through a C atom from the triazolylidene ligand and an additional chlorido ligand (Figure 1). The bond angles $C_{Carbene}$−Au−Cl are in the range of 175.7−178.5° (Table 1). The Au−Cl bond lengths (2.276−2.295 Å) are longer than the Au−$C_{Carbene}$ distances (1.958−2.001 Å), and the distances of both types of bonds are consistent with distances reported for related complexes in the literature.[5f,12a,16] The bond lengths within the triazolylidene rings point to a delocalized situation within those rings (Table S3 in the Supporting Information). The angle at the carbene-C atom is between 101 and 104° in all the complexes (Table S5 in the Supporting Information). In both complexes **1** and **2**, the bulky Dipp substituents on the triazolylidene rings sterically encumber the gold(I) centers, with this effect being more prominent in complex **1**, where the triazolylidene ring contains two Dipp substituents (Figure 1).

For the dinuclear complexes **5** and **6**, the coordination at the gold(I) centers is similar to that observed for the mononuclear complexes (Figure 1). In complex **6** the molecular structure in the crystal possesses an inversion center, making half of the molecule equivalent to the other half. The bond lengths and bond angles in **5** and **6** are similar to those discussed for the mononuclear complexes above (Tables S3−S7 in the Supporting Information). In the dinuclear complexes **5** and **6** the 1,2,3-triazolylidene rings within the di-1,2,3-triazolylidene ligands are twisted with respect to each other (Figure 1). This twist for complex **5** (61.9°) is less than half in comparison to that for complex **6** (122.1°). Accordingly, the Au−Au distance of 4.1 Å in **5** is shorter than the corresponding distance of 6.2 Å in **6** and both these distances exceed the sum of the van der Waals radii for two gold centers (2 × 1.66 Å).[16] Short metal−metal distances are often observed in dinuclear coinage-metal complexes with bicarbene ligands, and these distances are often taken as an indication of metallophillic interactions. However, in many such cases, the metal centers are coordinated to two bicarbene ligands (in contrast to one bicarbene for the cases discussed here), forcing them to approach each other in close proximities. As is seen from the discussion above, for complexes where the ligands do not enforce the metal centers to come close together, the distances (even in the case of gold) can be large, with no indications of any aurophilic interactions. Thus, a simple correlation of bond lengths and metalophilic interactions, without taking the geometry enforced by the ligands into consideration, probably should never be made. Theoretical calculations are often helpful for solving such dilemmas. To the best of our knowledge, **5** and **6** are only the second examples where structures from single-crystal X-ray diffraction have been presented for dinuclear gold(I) complexes with bitriazolylidene ligands.

These are also the first examples of crystal structure of digold(I) complexes that contain additional chlorido ligands on the gold centers. The structures of **5** and **6** are thus likely to serve as benchmarks for future work that might deal with aurophilic interactions in digold(I) complexes with bi-MIC ligands.

Catalysis. Gold(I) catalysts are known to play an important role in organic synthesis and in retrosynthetic analysis.[13a,17] Because of the Lewis acidic nature of the gold(I) center, they are able to activate π systems, such as alkynes.[13c] Gold(I) triazolylidene complexes were shown to be effective catalyst precursors for the synthesis of oxazolines.[12a,h] It was reported that such catalysts can perform the aldol condensation of isocyanoacetate and aldehydes to generate oxazolines. Formation of ligand-free gold clusters was observed in that case through gold(I)−triazolylidene bond cleavage during catalysis. Accordingly, no great influence of the substituents on the triazolylidene ligands was observed on the catalytic reaction rates. Another possibility of synthesizing oxazolines is the catalytic cyclization of propargylic amides. Gold(I) complexes containing phosphines or N-heterocyclic carbenes (NHCs) are known to act as catalysts for this kind of cyclization reaction.[18] To the best of our knowledge, there is just one report of catalysis of cyclization of propargylic amides with a gold(I) triazolylidene complex.[15] In general, gold(I) phosphine complexes have been used as catalysts for this transformation with only a few examples known for gold(I) N-heterocyclic carbene complexes.[18] As the fate of a metal complex during catalysis is usually dependent on all other components in the catalytic mixture, we were interested in testing gold(I) triazolylidene complexes as (pre)catalysts for the aforementioned reaction. In doing so, we wanted to decipher if gold(I) complexes containing different substituents on the triazolylidene ligands show different activities for that catalytic reaction. In addition, we were also interested in testing copper(II) salts as viable additives for silver(I) salts in the gold(I)-catalyzed cyclization of propargylic amides.

The catalytic activity of our new mono- and dinuclear gold(I) triazolylidene complexes were tested in the cyclization reaction of *N*-(2-propyn-1-yl)benzamide (**7**) to 2-phenyl-5-vinylidene-2-oxazoline (**8**) (Table 2). To optimize the reaction conditions for this cyclization reaction, we selected complex **4** as a (pre)catalyst. The reactions were performed at room temperature with a complex loading of 1 mol % in dichloromethane (Table 2). Complex **4** itself turned out to be a weakly active catalyst (conversions were low, 25% after 62 h; see entry 1, Table 2). By addition of $AgSbF_6$ (1 mol %) or $Cu(OTf)_2$ (5 mol %) almost quantitative conversions were reached within the same time. After 23 h the conversion had already reached 70% and 60%, respectively (entries 4 and 5, Table 2). Control experiments were performed to prove the catalytic inactivity of the additives themselves (entries 2 and 3, Table 2).

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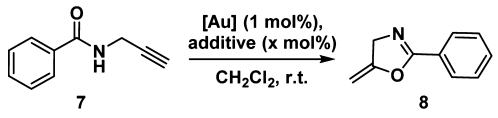
Table 2. Catalytic Activity of Gold(I) MIC Complex 4 in Combination with Different Additives[a]

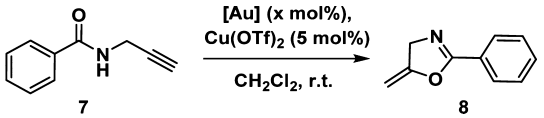


7 8

entry	[Au]	additive/amt (mol %)	time (h)	conversion (%)[b]
1	**4**		62	25
2		$AgSbF_6$/1	23	0
3		$Cu(OTf)_2$/5	23	5
4	**4**	$AgSbF_6$/1	23	70
			62	94
5	**4**	$Cu(OTf)_2$/5	23	60
			62	92

[a]Reaction conditions: *N*-(2-propyn-1-yl)benzamide (0.1 mmol), catalyst **4** (1 mol %), additive (1 mol % for [Ag], 5 mol % for [Cu]), and dichloromethane (1 mL), room temperature. [b]Conversions determined by ^{1}H NMR spectroscopy with hexadecane as internal standard.

Table 3. Catalytic Activity of Different Mono- and Digold(I) MIC Complexes[a]



7 8

			conversion (%)[b]			
entry	[Au]	loading (mol %)	1 h	4 h	7 h	25 h
1	**1**	1	20	60	80	98
2	**2**	1	20	50	70	95
3	**3**	1	20	30	40	80
4	**5**	0.5	20	55	75	98
5	**6**	0.5	15	25	30	50

[a]Reaction conditions: *N*-(2-propyn-1-yl)benzamide (0.2 mmol), catalyst (1 mol % for **1**–**3**, 0.5 mol % for **5** and **6**), $Cu(OTf)_2$ (5 mol %) and dichloromethane (2 mL), room temperature. [b]Conversions determined by ^{1}H NMR spectroscopy with hexadecane as internal standard.

In 2013, it was first reported that copper salts can work as additives instead of silver(I) salts in catalysis with gold(I) complexes.[14a,b] Silver(I) salts seem to abstract the Cl^- ligand of the gold(I) complexes [LAuCl] in a fast and irreversible manner. The reaction of these [LAuCl] species with other additives such as $Cu(OTf)_2$ are potentially reversible. This could be the reason for the longer lifetime of the catalytically active species $[LAu]^+$, because it cannot decompose that quickly. Another advantage of the use of $Cu(OTf)_2$ is found in preparative applications. In contrast to $Cu(OTf)_2$, silver(I) salts are usually more sensitive toward moisture and light.

As a consequence of these assumptions and the fact that the choice of the additive does not have a great effect on the conversions of *N*-(2 propyn-1-yl)benzamide (**7**) (entries 4 and 5, Table 2), we used $Cu(OTf)_2$ as an additive for further catalytic investigations.

To determine the catalytic activity of the different gold(I) MIC complexes **1**– **6**, a series of experiments were performed. The complex loading was set to 1 mol % for the mononuclear gold(I) complexes and 0.5 mol % for the dinuclear gold(I) complexes. Surprisingly, for all complexes **1**–**6** about the same catalytic activity could be observed after 1 h; 20% conversions were reached for each complex, except for complex **6** (entry 5, Table 3). However, already after 4 h the conversions clearly differ from each other. Complexes **1** and **5** gave the best conversions at 60% and 55%, respectively (entries 1 and 4, Table 3), followed by complex **2** with 50% conversion (entry 2, Table 3). Complexes **3** and **6** are less active than the other complexes with 30% and 25% conversion after 4 h (entries 3 and 5, Table 3). Interestingly, all complexes show high catalytic activity in the initial time of the reaction, but after some hours conversions decrease rapidly (Figure 2). To get an idea about the nature of the catalytic reaction, we added excess Hg(0) to the reaction mixture (with complex **4**) and we did not observe a decrease in conversion to product **8**. Hence, the active catalyst was unaffected and the cyclization reaction seems to be homogeneous for our catalysts. This observation excludes the operation of gold nanoparticles as active catalysts. However, as can be seen from Figure 2, the product formation is quite fast during the first hours of the catalytic reaction and then becomes rather slow for all cases. This might be an indication that the catalyst remains active and homogeneous over the first hours

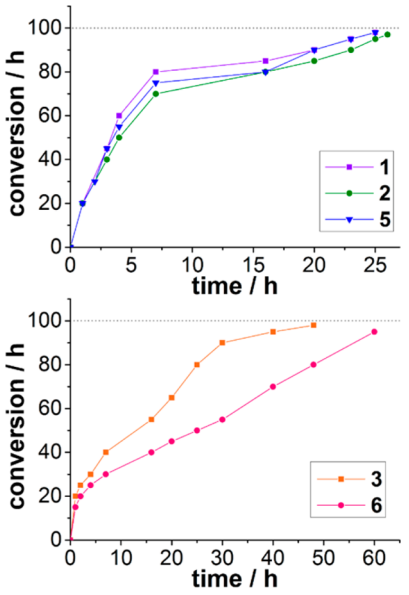


Figure 2. Time–conversion profiles for mono- and digold(I) complexes **1**–**6**: (top) complexes with Dipp substituent; (bottom) complexes with Mes substituent. Results presented are the average of at least three runs. The largest deviation observed from one run to the other was about 7% in the worst case.

and then eventually decomposes and becomes inactive. Finally, almost full conversions were obtained after 25–27 h for complexes **1**, **2**, and **5**, after 48 h for complex **3**, and after 60 h for complex **6** (Table 3); these times are similar to the time required for full conversion with complex **4** (entry 5, Table 2).

Complexes **1**, **2**, and **5** contain bulky Dipp groups as substituents at the triazolylidene rings. For these complexes, full conversions could be reached in half the time in comparison to complexes **3** and **6**, which have less sterically demanding Mes groups as substituents (Table 3). This suggests that the catalytic activity of the complexes **1**–**6** is dependent on the steric bulk of the substituents of the triazolylidene ligands (Figure 2). Complexes **1** and **5**, in which the triazolylidene-rings are substituted with two Dipp groups, are the most active (pre)catalysts. Complex **2** is almost as active as **1** and **5**. Replacement of one Dipp substituent from complex **1** for one

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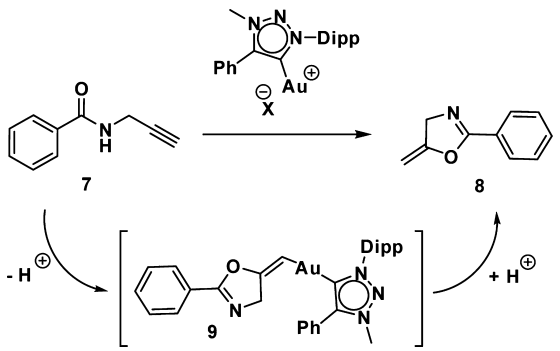
Ph group at the triazolylidene ring in complex **2** does not lead to a significant decrease in catalytic activity. Complexes **3** and **6** are less catalytically active, likely due to the less bulky Mes substituents at the triazolylidene rings. These results lead to the conclusion that the more sterically demanding the substituents on the triazolylidene rings, the higher the activity of the catalysts. Also worth noting is that mono- and dinuclear complexes containing the same substituents on the ligands result in almost the same conversions. While these data show that both the gold centers in complexes **5** and **6** are catalytically active, the data also point to a lack of cooperativity between the metal centers during catalytic turnover (Table 3). These results are perhaps not very surprising, considering the large gold−gold distances reported above as well as the need for only one metal center for catalytic turnover for the investigated reactions. The best catalysts presented here deliver close to quantitative product formation for the cyclization of propargyl amides with only 1 mol % catalyst loading with copper(II) salts as additives. The phosphine and N-heterocyclic gold(I) complexes reported in the literature require anywhere between 1 and 5 mol % catalyst loading, sometimes higher temperatures, and always silver salts as activators for catalyzing the same reaction.[18a,d,e,g] Hence, the catalysts presented here belong to the league of the best gold(I) catalysts known for this reaction.

Finally, we were interested in the mechanistic aspects of this cyclization reaction. For Au NHC complexes, it was possible to isolate gold(I) vinyl intermediates, which were obtained from the stoichiometric reaction of different propargylic amides with the in situ generated [IPrAu$^+$] species.[19] These Au NHC vinyl complexes are thought to be critical intermediates in the gold(I) NHC induced formation of oxazolines. To date, these kinds of gold(I) vinyl complexes are only known with the bulky 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) NHC ligand. Inspired by this, we wanted to try to identify this species with our gold(I) triazolylidene complexes (Scheme 2).

Scheme 2. Proposed Reaction Process for the Cyclization of *N*-(2-Propyn-1-yl)benzamide (7) to 2-Phenyl-5-vinylidene-2-oxazoline (8)



To achieve this, we mixed the gold(I) complex **2** with AgOTs in stoichiometric amounts in dichloromethane followed by addition of *N*-(2-propyn-1-yl)benzamide (**7**) and NEt_3 as base. The product **9** was seen to be formed according to the ESI-MS and ^{1}H and COSY NMR spectra. The ESI-MS showed the molecular peak corresponding to the monoprotonated form of **9** (Figure 3). The proton signals (d) of the CH_2− group in the oxazoline ring appear at 4.04 ppm in the ^{1}H NMR spectrum (Figure 4). The signal (s) for the vinyl proton CH close to the Au atom appears in the aromatic region at 7.45 ppm, according

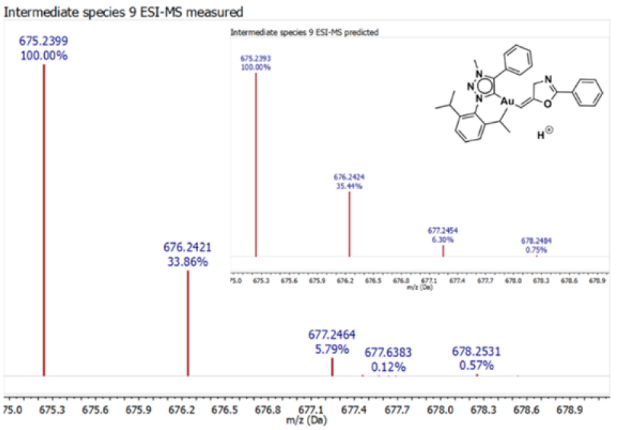


Figure 3. Measured and predicted ESI-MS for intermediate gold(I) MIC vinyl species **9**.

to the COSY NMR spectrum. This indicates that the protons of the CH_2− group couple with the vinyl proton (Figure 4). Chemical shifts for this vinyl proton vary in the literature from 6.08 to 6.72 ppm with the IPr ligand.[19a,c] Due to the triazolylidene ligand, the signal of the vinyl proton could be shifted to low field in the ^{1}H NMR spectrum, as it is in our case. Additionally, NOESY and GOESY NMR spectra (Figure 4 and Figures S13 and S14 in the Supporting Information) prove the existence of this intermediate. With these results in hand, we assume that formation of the gold(I) vinyl species **9** was successful and this species is an intermediate in the catalytic reaction leading to the formation of 2-phenyl-5-vinylidene-2-oxazoline (**8**) (Scheme 2).

CONCLUSION

In summary, we have presented here the synthesis and characterization of three new mononuclear gold(I) MIC complexes and the first examples of the synthesis and structural characterization through X-ray diffraction of novel dinuclear gold(I) MIC complexes that contain additional chlorido ligands on the gold centers. For the digold(I) complexes relatively large Au−Au distances were observed in the solid state, precluding the existence of aurophilic interactions in these complexes. All complexes are active precatalysts for the synthesis of 2-phenyl-5-vinylidene-2-oxazoline. The catalytic reactions could be performed under silver(I)-free conditions. Copper(II) triflate was found to be a viable additive for catalysis using these gold(I) triazolylidene complexes. We have shown that the ligand structure has a direct influence on the catalytic activity of the complexes. The complexes with the bulky diisopropylphenyl substituents display significantly higher activity in contrast to the complexes with the less sterically demanding mesityl substituents. In general, no significant differences have been observed in the activity of the mono- and dinuclear complexes with the same substituents on the ligands, thus showing the lack of catalytic cooperativity for the present case. We were also able to detect the vinylgold(I) species, which is an intermediate in the catalytic reaction process of the chosen cyclization reaction. This species could be verified by mass spectrometry and ^{1}H and COSY NMR spectroscopy. These kinds of gold(I) MIC complexes can be useful precatalysts for a host of other organic transformations. In contrast to several reports where the steric bulk on the triazolylidene ligand was shown to be irrelevant for various catalytic transformations,[10b,f,g,k,l,o,12h,20] our results here indicate that the

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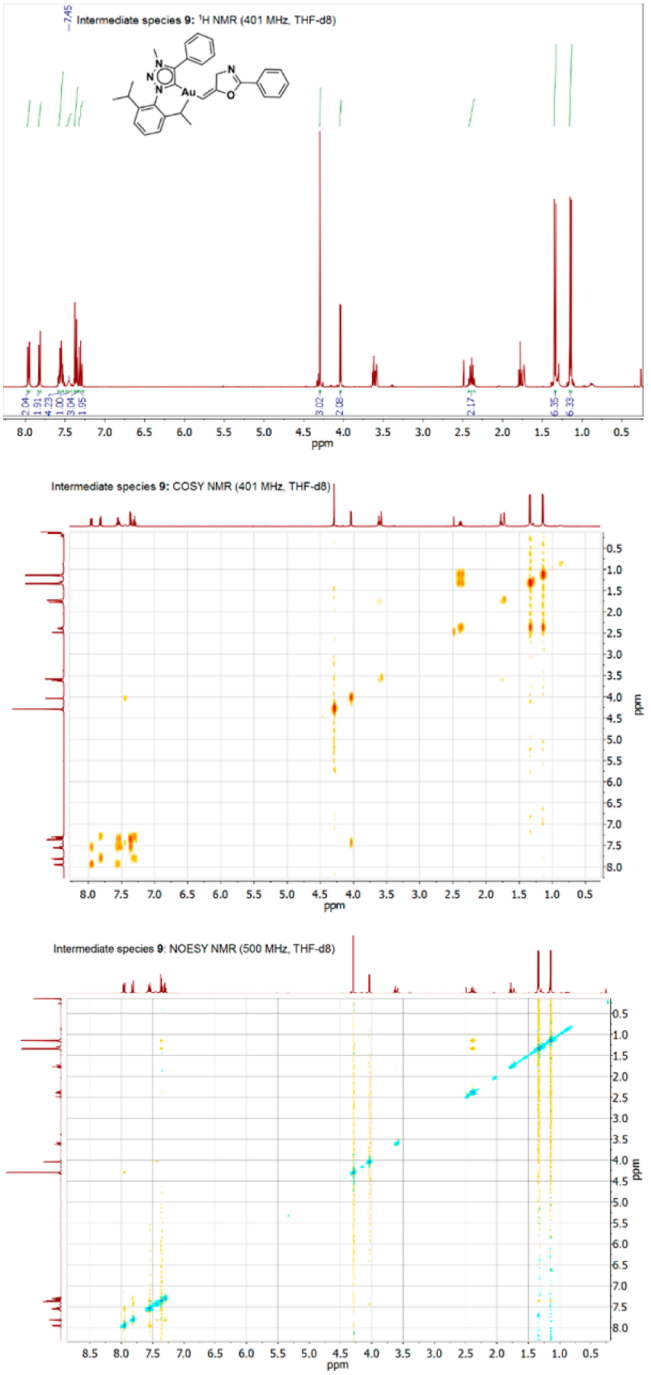

Figure 4. ^{1}H NMR spectrum (top), COSY NMR spectrum (middle) at 401 MHz, and NOESY NMR spectrum (bottom) at 500 MHz for the intermediate gold(I) MIC vinyl species **9**.

substitutions on the triazolylidene rings do play a role in catalytic rate enhancement for the gold(I) triazolylidene induced formation of oxazolines. Thus, fine tuning of the steric properties of such MIC ligands might lead to more active catalysts for other processes as well.

EXPERIMENTAL SECTION

General Procedures, Materials, and Instrumentation. AuCl(SMe$_2$),[21] TBTA,[22] *N*-(2-propyn-1-yl)benzamide,[23] 2-azido-1,3-diisopropylbenzene,[10e] the triazolium salts [**HL4**]**I**,[24] [**HL3**]**I**,[10b] [**HL1**]**I**,[8f] [**H$_2$L5**](**BF$_4$**)$_2$, and [**H$_2$L6**](**BF$_4$**)$_2$,[8g] and the complex **3**[12a] were prepared as described previously in the literature. The triazole **L2** was also described previously in the literature,[4] but the synthesis was modified.[5e] Commercially available chemicals were used as purchased, unless otherwise noted. The solvents used for synthesis and catalysis were dried and distilled under inert gas and degassed by common techniques prior to use, unless otherwise noted. Column chromatography was performed over Silica 60 M (0.04−0.063 mm). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL ECS 400, JEOL ECZ 400, or JEOL ECX 400 spectrometer. Chemical shifts are reported in ppm with reference to the residual solvent peaks. Multiplets are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sept (septet), m (multiplet), and combinations thereof. Mass spectrometry was performed on an Agilent 6210 ESI-TOF instrument.

X-ray data were collected on a Bruker Smart AXS or Bruker D8 Venture system. Data were collected between 100(2) and 293(2) K (see Table S1 in the Supporting Information) using graphite-monochromated Mo Kα radiation ($\lambda\alpha$ = 0.71073 or 0.71069 Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard ψ−ω scan techniques and were scaled and reduced using Saint+ and SADABS software. The structures were solved by direct methods using SHELXS-97 or SHELXS_2014/7 and refined by full-matrix least squares, refining on F^2. Non-hydrogen atoms were refined anisotropically.[25] If it is noted, bond lengths and angles were measured with Diamond Crystal Version 4.0.2 and Molecular Structure Visualization Version 3.1. CCDC 965897, 1482518, 1482519, 1482516, and 1482517 contain the crystallographic data for this work.

Preparation of 1-(2,6-Diisopropylphenyl)-4-phenyl-1*H*-1,2,3-triazole (L2). The triazole **L2** was described previously in the literature,[4] but the synthesis was modified.[5e] To phenylacetylene (1 equiv, 306 mg, 3.00 mmol), 2-azido-1,3-diisopropylbenzene (1 equiv, 609 mg, 3.00 mmol), copper(II) sulfate pentahydrate (0.05 equiv, 36.9 mg, 0.150 mmol), sodium ascorbate (0.2 equiv, 119 mg, 0.600 mmol), and TBTA (0.01 equiv, 15.9 mg, 0.0300 mmol) was added a dichloromethane/water/*tert*-butyl alcohol mixture (5 mL/10 mL/10 mL). The reaction mixture was heated for 2 days at 55 °C. After the mixture was cooled to room temperature, a solution of EDTA sodium salt in water/ammonia (30 mL/30 mL) was added, and the product was extracted with dichloromethane (4 × 50 mL). The combined organic phases were dried with sodium sulfate and filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography over silica gel by using a gradient from 0 to 10% acetone in dichloromethane. The product was obtained as a light yellow solid in a yield of 77% (709 mg, 2.32 mmol).

Preparation of 1-(2,6-Diisopropylphenyl)-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium Iodide ([HL2]I). **L2** (1 equiv, 709 mg, 2.23 mmol) was dissolved in acetonitrile (4.5 mL, c = 0.5 mol L^{-1}), and methyl iodide (20 equiv, 2.86 mL, 46.0 mmol) was added. Then the mixture was heated to reflux for 2 days. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane (5 mL) and precipitated with diethyl ether (50 mL). The colorless precipitate was collected by filtration and washed with diethyl ether. The product was obtained in a yield of 69% (720 mg, 1.61 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethane/diethyl ether (2/1) at room temperature. ^{1}H NMR (401 MHz, CDCl$_3$, 20 °C): δ 8.79 (s, 1H, triazolium-*H*), 8.10−8.06 (m, 2H, aryl-*H*), 7.65−7.58 (m, 4H, aryl-*H*), 7.37 (d, $^{3}J_{H,H}$ = 7.9 Hz, 2H, aryl-*H*), 4.63 (s, 3H, N-C*H*$_3$), 2.50 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 2H, 2 × C*H*), 1.22 (m, 12H, 4 × C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 20 °C): δ 145.7, 144.5 (both C$_{trz}$), 133.1, 132.4, 130.8, 130.7, 130.6, 129.8, 124.9, 121.2 (all aryl-*C*), 41.2 (N-CH$_3$), 29.0, 24.7, 24.2 (all alkyl-*C*). HRMS (ESI): calcd for [C$_{21}$H$_{26}$N$_3^+$] ([M − I]$^+$) m/z 320.2122, found 320.2135.

General Procedure for the Preparation of the Monogold(I) Carbene Complexes. A mixture of the triazolium salt [**HL1**]**I** or [**HL2**]**I** (1 equiv, 0.100 mmol), silver(I) oxide (1.5 equiv, 34.8 mg, 0.150 mmol), potassium chloride (2 equiv, 14.9 mg, 0.200 mmol), and cesium carbonate (3 equiv, 97.8 mg, 0.300 mmol) in absolute acetonitrile (10 mL) was stirred at room temperature under exclusion of light. After 3 days the reaction mixture was filtered over Celite

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under an N_2 atmosphere and volatiles were removed under high vacuum. The residue was dissolved in a mixture (1/1) of absolute dichloromethane and acetonitrile (10 mL), and $AuCl(SMe_2)$ (1 equiv, 29.5 mg, 0.100 mmol) was added. After it was stirred for 24 h at room temperature, the reaction mixture was filtered over Celite and the solvent was evaporated. The residue was redissolved in dichloromethane (5 mL), precipitated with pentane (50 mL), and filtered. The precipitate was collected by filtration and passed through a short pad of SiO_2, and this pad was eluted with dry CH_2Cl_2. After evaporation of the solvent and precipitation again, the pure complexes were obtained as colorless solids. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the complex in dichloromethane at room temperature.

Preparation of the Gold(I) Carbene Complex ***1***. The product was obtained as a colorless solid or crystals in a yield of 33% (21.0 mg, 0.033 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.56 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, aryl-*H*), 7.55 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, aryl-*H*), 7.31 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, aryl-*H*), 7.31 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, aryl-*H*), 3.91 (s, 3H, N−CH_3), 2.44 (sept, $^3J_{H,H}$ = 6.9 Hz, 2H, 2 × C*H*), 2.35 (sept, $^3J_{H,H}$ = 6.9 Hz, 2H, 2 × C*H*), 1.36−1.31 (m, 12H, 4 × CH_3), 1.25−1.19 (m, 12H, 4 × CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 21 °C): δ 164.2 (carbene-*C*), 149.0 (C_{trz}), 145.0, 145.0, 135.2, 132.0, 131.7, 124.4, 123.9, 122.5 (all aryl-*C*), 37.3 (N-CH_3), 31.8, 29.1, 25.1, 24.3, 24.1, 23.4 (all alkyl-*C*). HRMS (ESI): calcd for $[C_{27}H_{37}AuN_3^+][(M - Cl)^+]$ *m*/*z* 600.2648, found 600.2659. Anal. Calcd for $C_{27}H_{37}AuClN_3$: C, 50.99; H, 5.86; N, 6.61. Found: C, 50.98; H, 5.92; N, 6.65.

Preparation of the Gold(I) Carbene Complex ***2***. The product was obtained as a colorless solid or crystals in a yield of 50% (28.0 mg, 0.051 mmol). ^{1}H NMR (501 MHz, $CDCl_3$, 22 °C): δ 7.81−7.78 (m, 2H, Ar-*H*), 7.56−7.52 (m, 4H, aryl-*H*), 7.29 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, aryl-*H*), 4.23 (s, 3H, N−CH_3), 2.31 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H, C*H*), 1.34−1.32 (m, 6H, 2 × CH_3), 1.15−1.14 (m, 6H, 2 × CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 23 °C): δ 146.8, 145.2 (C_{trz}), 135.1, 131.6, 130.6, 129.8, 129.3, 126.0, 124.4 (all aryl-*C*), 38.4 (N-CH_3), 28.9, 24.5, 24.2 (all alkyl-*C*). The carbene-C is not visible in this ^{13}C{^{1}H} NMR spectrum. HRMS (ESI): calcd for $[C_{21}H_{25}AuClN_3][(M + Na)^+]$ *m*/*z* 574.1295, found 574.1312. Anal. Calcd for $C_{21}H_{25}AuClN_3$: C, 45.70; H, 4.57; N, 7.61. Found: C, 45.88; H, 4.76; N, 7.66.

Preparation of the Gold(I) Carbene Complex 4. A mixture of [**HL4**]**I** (1 equiv, 113 mg, 0.300 mmol) and silver(I) oxide (0.5 equiv, 34.8 mg, 0.150 mmol) was stirred in absolute dichloromethane (30 mL) at room temperature for 17 h under exclusion of light. Then $AuCl(SMe_2)$ (1 equiv, 88.4 mg, 0.300 mmol) was added. After the mixture was stirred for another 24 h at room temperature under exclusion of light, the reaction mixture was filtered over Celite and washed with dichloromethane and the solvent was evaporated. The residue was redissolved in dichloromethane (3 mL) and precipitated with pentane (100 mL). The precipitate was collected by filtration and passed through a short pad of SiO_2, and this pad was eluted with dry CH_2Cl_2. Evaporation of the solvent and precipitation again gave complex **4** as a colorless solid in a yield of 82% (124 mg, 0.244 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.78−7.74 (m, 2H, aryl-*H*), 7.58−7.54 (m, 3H, aryl-*H*), 7.00 (s, 2H, aryl-*H*), 4.23 (s, 3H, N-CH_3), 2.36 (s, 3H, CH_3), 2.07 (s, 6H, 2 × CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 160.6 (carbene-*C*), 147.2, 140.8, 135.6, 134.3, 130.6, 129.8, 129.6, 129.4, 126.2 (all aryl-*C*), 38.2 (N-CH_3), 21.6, 17.8 (all alkyl-C). HRMS (ESI): calcd for $[C_{18}H_{19}AuClN_3][(M + Na)^+]$ *m*/*z* 532.0825, found 532.0801. Anal. Calcd for $C_{18}H_{19}AuClN_3{\cdot}C_5H_{12}$: C, 47.47; H, 5.37; N, 7.22. Found: C, 47.43; H, 5.05; N, 7.48.

General Procedure for the Preparation of the Digold(I) Carbene Complexes. A mixture of the bitriazolium salt [$\mathbf{H_2L5}$]-($\mathbf{BF_4}$)$_2$ or [$\mathbf{H_2L6}$]($\mathbf{BF_4}$)$_2$ (1 equiv, 0.100 mmol), silver(I) oxide (5 equiv, 116 mg, 0.500 mmol), potassium chloride (4 equiv, 29.8 mg, 0.400 mmol), and cesium carbonate (6 equiv, 196 mg, 0.600 mmol) in absolute acetonitrile (10 mL) was stirred at room temperature under exclusion of light. After 3 days the reaction mixture was filtered over Celite under a N_2 atmosphere and volatiles were removed under high vacuum. The residue was dissolved in a mixture (1/1) of absolute dichloromethane and acetonitrile (15 mL), and $AuCl(SMe_2)$ (2 equiv, 58.9 mg, 0.200 mmol) was added. After it was stirred for 24 h at room temperature, the reaction mixture was filtered over Celite and the solvent was evaporated. The residue was redissolved in dichloromethane (5 mL), precipitated with pentane (50 mL), and filtered. The precipitate was collected by filtration and passed through a short pad of SiO_2, and this pad was eluted with dry CH_2Cl_2. After evaporation of the solvent and precipitation again, the pure complexes were obtained as colorless solids.

Preparation of the Digold(I) Carbene Complex ***5***. The product was obtained as a colorless solid or crystals in a yield of 23% (44.0 mg, 0.046 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile at room temperature. ^{1}H NMR (401 MHz, CD_2Cl_2, 21 °C): δ 7.69−7.65 (m, 2H, aryl-*H*), 7.44−7.38 (m, 4H, aryl-*H*), 4.57 (s, 6H, 2 × N-CH_3), 2.46 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H, 2 × C*H*), 2.12 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H, 2 × C*H*), 1.38−1.36 (m, 12H, 4 × CH_3), 1.21−1.19 (m, 12H, 4 × C*H*). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 21 °C): δ 166.5 (carbene-*C*), 146.2 (C_{trz}), 145.4, 135.2, 133.3, 132.6, 125.5, 124.9 (all aryl-*C*), 40.9 (N-CH_3), 29.7, 29.4, 24.8, 24.3 (all alkyl-*C*). HRMS (ESI): calcd for $[C_{30}H_{40}Au_2ClN_6^+][(M - Cl)^+]$ *m*/*z* 913.2329, found 913.2316. Anal. Calcd for $C_{30}H_{40}Au_2Cl_2N_6$: C, 37.95; H, 4.25; N, 8.85. Found: C, 37.96; H, 4.53; N, 8.90.

Preparation of the Digold(I) Carbene Complex ***6***. The product was obtained as a colorless solid or crystals in a yield of 15% (26.0 mg, 0.030 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the complex in dichloromethane at room temperature. ^{1}H NMR (401 MHz, CD_2Cl_2, 20 °C): δ 7.13 (s, 2H, aryl-*H*), 7.12 (s, 2H, aryl-*H*), 4.54 (s, 6H, N−CH_3), 2.42 (s, 6H, 2 × CH_3), 2.14 (s, 6H, 2 × CH_3), 2.09 (s, 6H, 2 × CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 21 °C): δ 164.7 (carbene-*C*), 141.8 (C_{trz}), 135.0, 134.8, 133.5, 133.2, 130.2, 139.6 (all aryl-*C*), 40.3 (N-CH_3), 21.4, 18.2, 17.7 (all alkyl-*C*). HRMS (ESI): calcd for $[C_{24}H_{28}Au_2ClN_6^+][(M - Cl)^+]$ *m*/*z* 829.1390, found 829.1411. Anal. Calcd for $C_{24}H_{28}Au_2Cl_2N_6{\cdot}0.55C_5H_{12}$: C, 35.50; H, 3.85; N, 9.29. Found: C, 35.71; H, 3.53; N, 9.42.

General Procedure for the Catalytic Cyclization Reaction of *N*-(2-Propyn-1-yl)benzamide (7) To Give 2-Phenyl-5-vinylidene-2-oxazoline (8). To the complex (1 mol % for **1**−**4**, 0.5 mol % for **5** and **6**), $Cu(OTf)_2$ (5 equiv based on the amount of [Au]) or $AgSbF_6$ (1 equiv based on the amount auf [Au]), and *N*-(2-propyn-1-yl)benzamide (1 equiv, 31.8 mg, 0.200 mmol) was added absolute dichloromethane (2 mL). The reaction mixture was stirred at room temperature for the given time. Hexadecane (10 mol %) as internal standard was also added to the reaction mixture. Samples were taken after different reaction times. Samples were taken by removing 0.1 mL of the reaction mixture by syringe and diluting with $CDCl_3$ (0.5 mL) for analysis by ^{1}H NMR spectroscopy. Conversions were then calculated by comparing the integral of the CH_3 groups of the hexadecane with the integral of the CH_2 group of *N*-(2-propyn-1-yl)benzamide.

Preparation of the Gold(I) Intermediate Species 9. The procedure was followed in accord with the synthesis of similar complexes in the literature.[19a] A mixture of complex **2** (1 equiv, 12.1 mg, 0.022 mmol) and silver(I) *p*-toluenesulfonate (1 equiv, 6.14 mg, 0.022 mmol) in absolute dichloromethane (4 mL) was stirred at room temperature for 1 h. Then triethylamine (4.45 equiv, 0.0135 mL, 9.82 mg, 0.097 mmol, 13.6 μL) and *N*-(2-propyn-1-yl)benzamide (0.95 equiv, 3.34 mg, 0.021 mmol) were added. The reaction mixture was stirred for an additional 20 h at room temperature. Volatiles were removed under high vacuum. The residue was redissolved in absolute THF (2 mL) and filtered over a short plug of basic allox under an inert gas atmosphere. The plug was eluted with absolute THF (30 mL), and volatiles were removed under high vacuum. The product was obtained as a colorless foam. HRMS (ESI): calcd for $[C_{31}H_{34}AuN_4O^+][(M + H)^+]$ *m*/*z* 675.2393, found 675.2399.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00675.

Crystallographic details and NMR spectra (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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