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Synthesis and Catalytic Applications of Multinuclear Gold (I)-1,2,3-Triazolylidene Complexes

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A series of mono- to trinuclear gold(I) complexes (1–3) supported by oxo-functionalized 1,2,3-triazolylidenes have been prepared. All new compounds were fully characterized by means of ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, and in the case of complexes 1 and 2 by x-ray diffraction. The catalytic performance of the new triazolylidene gold complexes was tested in several hydroelementation and cyclization processes employing a variety of alkynes as starting materials. According to the overall results, the trinuclear complex 3 displayed the highest catalytic activity in all processes, providing good to excellent yields under mild reaction conditions.

Introduction

Since the discovery of bottleable N-heterocyclic carbenes (NHCs) in 1991, they have attracted extraordinary attention in homogeneous catalysis either as free-ligands or when coordinated to transition o main group metals.[1] Owing to their strong σ-donor capacity, air stability, and low toxicity, NHCs have been considered as ideal alternatives to the more commonly used phosphines and amino monodentate ligands.[2] Due to the particular features of these carbon-based species, the design and preparation of new types of NHC ligands is a constant effort in organometallic chemistry.

Mesoionic (MIC) 1,2,3-Triazolylidenes[2] are an important subclass of NHC ligands that has presented an exponential growth in recent years.[3] These type of ligands where the carbene center is not flanked by heteroatoms in both sides of their structures, have attracted a great deal of attention as they display enhanced σ-donor properties compared to classical N-heterocyclic carbenes while, their mesoionic character improves their ability to stabilize different oxidation states.[4] Their 1,2,3-triazolium precursors, can be easily prepared by means of the copper(I) catalyzed "click" cycloaddition of alkynes and azides[5] (CuAAC) and their subsequent N-alkylation.[6] Because of the ease in structural modification in the triazolylidene frameworks, great topological diversity is achieved by modification of the substituent appended at the N1-, N3- and C4-positions. This level of substitution strongly affects the electronic and steric properties of the resulting mesoionic carbenes and their respective metal complexes.

In general, the coordination chemistry of 1,2,3-triazolylidenes is dominated by monotopic species.[7] The development and preparation of ligand platforms allowing the generation of di-[8] trinuclear[9] and tetranuclear metal complexes[10] based on MICs have been reported recently in the literature. Along with the increasing interest on developing cleaner chemical processes, particular attention has targeted the design and synthesis of multinuclear metal complexes as they usually display enhanced reactivity and selectivity over their monometallic counterparts.[11] A number of these multinuclear complexes have demonstrated to be highly efficient as catalysts for a variety of chemical reactions including several cross coupling processes, hydroaminations, olefin polymerizations, among others.[12] The improvement in the catalytic and selectivity achieved by these catalysts is attributed mainly to cooperative interactions between proximal metal centers where features such as intermetallic distances, three-dimensional structures, and the enhanced probability of interaction with the substrates play a key role.[13]

In line with our interest in multimetallic complexes for catalytic applications, we report herein the preparation and full characterization of a series of mono- to tri-triazolylidene gold complexes (1–3) which are obtained by the one step treatment of triazolium precursors (I–III) with KHMDS in presence of the $AuCl(SMe_2)$. Complexes 1–3 were tested in the hydration and hydroamination of terminal alkynes and in the preparation of oxazolines by the cyclization of propargylic amines. In all catalytic processes, the trinuclear complex 3 displayed the best performance of the series, suggesting cooperative effects in the multinuclear complexes. Details of the full characterization of the new complexes and their catalytic comparison will be discussed.

Results and Discussion

The synthesis of the 1,2,3-triazolium salt precursors I–III was performed according to the literature procedure by means of a copper catalyzed cycloaddition (CuAAC) of mesityl azide with the appropriate alkyne, followed by N-quaternarization with

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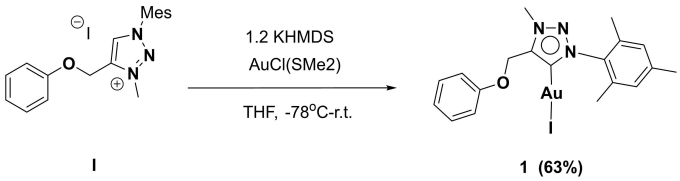
methyl iodide.[14] A comparison of the sigma-donation of the MIC salts I–III, using the already available $^{1}J_{CH}$ coupling constants from 1H NMR spectra was obtained.[14b] The coupling values for I (202.76 Hz), II (201.81 Hz) and III (200.42 Hz) are consistent with a higher σ-donation compared to classical NHC ligands (208–223 Hz). In order to get access to the desired gold (I) triazolylidene complexes, we initially tested the reaction of the triazolium salt I with slight excess of potassium hexamethyldisilazane (1.3 equiv.) and one equivalent of $AuCl(SMe_2)$ in THF at −78 °C. After work up and purification by column chromatography, complex 1 was isolated in 63 % yield as an air stable yellow solid (Scheme 1). Our attempts to generate complex 1 by the reaction of triazolium I with Ag_2O and the subsequent addition of $AuCl(SMe_2)$ resulted in yields lower than 35 %.



Scheme 1. Synthesis of triazolylidene complex 1.

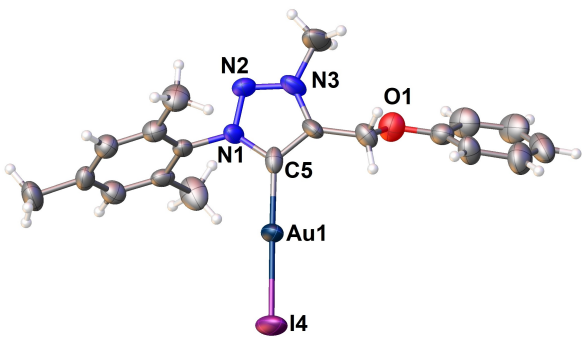


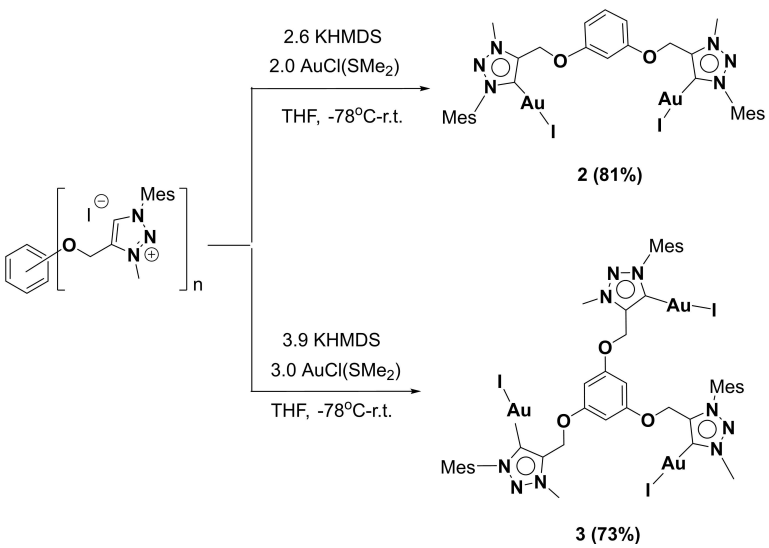
Figure 1. Molecular structure of the of complex 1. Ellipsoids are shown at 50 % probability.

NMR spectroscopy studies confirmed the formation of complex 1 by the disappearance of the acidic CH+ proton in the ^{1}H-NMR spectra (around 9 ppm) and the observation of a low field signal at 173.2 ppm in ^{13}C NMR, corresponding to the carbenic carbon bound to gold. To gain further insight into the structural features of complex 1, single crystals were grown from a mixture of dichloromethane-THF at room temperature (Figure 1).

Complex 1 crystallizes in the triclinic system with the *P*-1 space group, and the monomeric structure display a carbene-gold bond distance of 2.028(11) Å and a Au–I bond distance of 2.5412(9) Å, which are in the range of recently reported MIC–Au analogues.[15] The coordination of the gold center to the triazolylidene and the iodine atom results in a slightly distorted linear geometry with a C5–Au1–I1 angle of 176.5(2)°, and no short contact with the phenoxy moiety is observed.

Motivated by the successful metalation of the monotriazolium salt I, we followed a similar strategy for the preparation of the multinuclear triazolylidene complexes. Thus, as shown in Scheme 2, the one-pot reaction of the triazolium salts II and III with excess of KHMDS and the required amounts of the $AuCl(SMe_2)$, produces complexes 2 and 3 in adequate yields (73–81 %). Purification of the complexes was achieved by chromatography column using a mixture of dicloromethane/ethanol as eluent and interestingly, despite of the high degree of metalation in complexes 2 and 3, all of them display excellent solubility in benzene, toluene and a variety of chlorinated solvents.

Characterization of complexes was achieved by NMR spectroscopy, melting point, and elemental analysis. As expected for complexes 2 and 3, the ^{1}H NMR spectra no longer display the acidic CH-imidazolium protons while, only one set of resonances for the N-methyl, methylene and mesityl are



Scheme 2. Synthesis of complexes 2 and 3.

observed. ^{13}C-NMR spectroscopy shows a single carbene-gold peak located at 173.1 and 173.2 for the di- and trinuclear complexes, respectively. Overall, the NMR patters of 2 and 3 are consistent with a C_2 and C_3 symmetry in solution, respectively, and discard the presence of conformational isomers.

Despite the numerous attempts to crystallize complexes 2 and 3, we were unsuccessful on obtaining appropriate x-ray quality samples. The best set of single crystals for complex 2 were obtained from the slow evaporation of a mixture of THF-dichloromethane yielding colorless needles. Although full refinement could not be obtained owing to the low quality of the crystals,[16] the molecular structure and atom connectivity of complex 2 is unambiguous and allow its discussion and comparison. As depicted in Figure 2, complex 2 crystallizes in the triclinic P-1 space group with the asymmetric unit displaying Au1–C1 and Au2–C2 bond distances of 2.07(2) and 2.16(3) Å similar to previously reported MIC–Au(I) complexes.[15] The metal centers display a slightly distorted linear geometry and likewise as observed in complex 1, no coordination via the oxygen atom is observed.

During the last two decades gold(I) complexes have demonstrated their excellent Lewis acidity for the selective activation of alkenes and alkynes under mild conditions.[17] In particular, NHC-based gold(I) complexes have shown applicability as precatalysts in various processes such as C–H bond functionalizations, cyclization of enynes, hydroaminations, hydrazination, cross-coupling reactions, among others.[18] Taking in consideration the hitherto documented enhanced catalytic performance of multinuclear complexes compared to their mononuclear analogues,[11] we proceeded to compare the catalytic efficiencies of complexes 1–3 in several gold(I)-catalyzed hydroelementation and cyclization processes.

As a first benchmark reaction, we chose the hydroamination of terminal alkynes with aniline derivatives for which several gold-carbene complexes have proved effective.[19] As depicted in Table 1, under neat conditions, the reaction between phenylacetylene and aniline for 6 h proceed smoothly at low temperature (40 °C), using 0.5 mol% of mononuclear catalyst 1 and $AgSbF_6$ (1 mol%) as halide scavenger. The reaction was also carried out using 0.25 mol% and 0.167 mol% of 2 and 3 (same amount of gold for both complexes), respectively, providing full

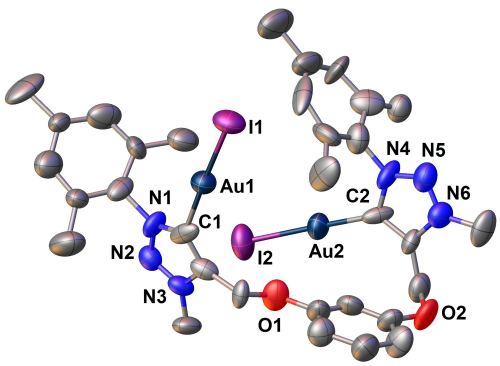
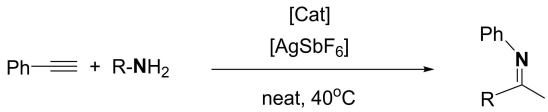


Figure 2. Molecular structure of the of complex 2. Ellipsoids are shown at 50% probability. Hydrogens omitted for clarity.

Table 1. Hydroamination of phenylacetylene with several aniline substrates.[a]



Entry	R	[Cat]	Conversion 6 h [%][b]	Conversion 3 h [%][b]
1	Ph	1	96	62
2	Ph	2	99	88
3	Ph	3	99	96
4	4-(OMe)Ph	1	69	48
5	4-(OMe)Ph	2	82	70
6	4-(OMe)Ph	3	93	88
7	4-(NO_2)Ph	1	87	55
8	4-(NO_2)Ph	2	92	78
9	4-(NO_2)Ph	3	95	91
10	2,4,6-(Me_3)Ph	1	70	46
11	2,4,6-(Me_3)Ph	2	84	77
12	2,4,6-(Me_3)Ph	3	96	92
13	2,6-(^{i}Pr)$_2$Ph	1	56	37
14	2,6-(^{i}Pr)$_2$Ph	2	81	66
15	2,6-(^{i}Pr)$_2$Ph	3	89	82

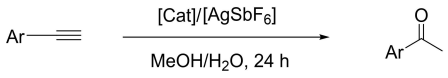
[a] Reaction conditions: Phenylacetylene (0.5 mmol), substituted aniline (0.55 mmol), catalytic system based in complex 1 (0.5 mol%)/$AgSbF_6$ (1.0 mol%); system based in complex 2 (0.25 mol%)/$AgSbF_6$ (0.5 mol%); system based in complex 3 (0.167 mol%)/$AgSbF_6$ (0.334 mol%). [b] Isolated yields as the average of two runs.

conversions to product in both cases. A decrease in reaction time to 3 h shows higher conversions for the di- (88%) and trinuclear complexes (96%) compared to the mononuclear complex 1 (62%). Furthermore, the trinuclear complex 3 proved to be the most effective precatalyst of the series converting challenging substrates such as bulky anilines (bearing the 2,4,6-timethyl and 2,4-diisopropylphenyl groups) into the desired products in good yields (entries 10–15).

The hydration of alkynes which provides the respective ketone derivatives, is a well-known an a highly valuable reaction in organic synthesis. In fact, several metals (mainly mercury salts) are known to catalyze the hydration of alkynes,[20] however, relatively harsh reaction conditions are usually required to achieve good yields.[21] The pivotal discovery of $HAuCl_4$ for alkyne hydration by Utimoto and coworkers[22] and of the more effective "cationic" gold-catalyzed alkyne hydration reactions[23] led to the seminal findings by Nolan[24] of highly efficient NHC-gold complexes for the hydration of terminal and internal alkynes. Motivated by high stability and success of NHC-gold complexes in the hydration of alkynes, we decided to conduct a comparative study of the catalytic performance between the multinuclear complexes 1–3 in this process. Hence, the hydration of phenylacetylene using the catalytic system MIC–Au(I)/$AgSbF_6$ salt in methanol was chosen as the model reaction.

As observed in Table 2, complexes 1–3 convert phenylacetylene into the corresponding ketone in yields above 90% (entries 1–3) when the reaction is carried out at 90 °C and with catalyst loadings of 3 mol% (based in the metal). A decrease of the temperature to 60 °C results in appreciable decrease of the yields for the mononuclear (44%) and dinuclear (69%) while,

Table 2. Hydration of phenylacetylene catalyzed by complexes 1–3.[a]



Entry	Ar	[Cat]	Conversion 90 °C [%][b]	Conversion 60° [%][b]
1	Ph	1	94	44
2	Ph	2	97	69
3	Ph	3	99	93
4	4-(Br)Ph	1	91	28
5	4-(Br)Ph	2	97	64
6	4-(Br)Ph	3	99	87
7	4-(OMe)Ph	1	74	23
8	4-(OMe)Ph	2	88	71
9	4-(OMe)Ph	3	93	86
10	4-(CF_3)Ph	1	49	18
11	4-(CF_3)Ph	2	69	57
12	4-(CF_3)Ph	3	87	82
13	2,4,6-(Me_3)Ph	1	69	55
14	2,4,6-(Me_3)Ph	2	82	71
15	2,4,6-(Me_3)Ph	3	95	90

[a] Reaction conditions: Phenylacetylene (1.0 mmol), water (4.0 mmol), catalytic system based in complex 1/$AgSbF_6$ (3.0 mol%, each); system based in complex 2/$AgSbF_6$ (1.5 mol%, each); system based in complex 3/$AgSbF_6$ (1.0 mol%, each); [b] Isolated yields as the average of two runs.

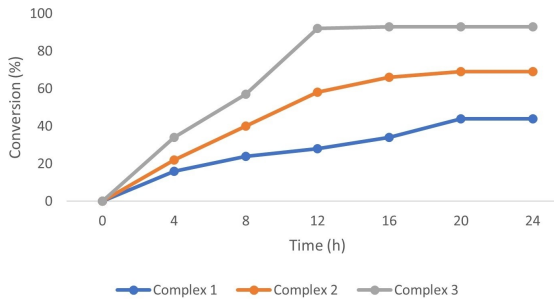


Figure 3. Hydration of phenylacetylene using precatalysts 1–3. Reactions carried out at 60 °C. Conversions determined by ^{1}H NMR spectroscopy based on the amount of phenylacetylene remaining in solution using mesitylene as internal standard.

the trinuclear complex 3 conserve its catalytic efficiency with a conversion of 93%. The trinuclear gold complex also shows the best performance of the series with more challenging substrates including 4-methoxy-, 4-trifluoromethane- and 2,4,6-trimetyl-substituted phenylacetylenes.

To get more insight into the catalytic behavior of the multinuclear gold complexes 1–3, the catalytic profiles for the hydration of phenylacetylene at 60 °C were performed with the reaction conditions presented in Table 2 (entries 1–3). As depicted in Figure 3, complex 3 reaches conversion over 50% after 4 h of reaction and its maximum conversion is observed in 12 h. In case of the bimetallic complex, the maximum conversion is reached after 16 h of reaction while, the conversion to products by complex 1 is much slower reaching maximum conversions after 20 h and remaining unchanged after that time.

The full set of results of the catalytic profiles suggest that the concentration of active species[25] provided by the multinuclear complex 3 has an important effect in the efficiency and stability of the catalytic species.

Triazolylidene-gold(I) complexes have shown to be efficient catalysts in the synthesis of oxazolines either by the cyclization of propargylic amides or the condensation of isocyanoacetate and aldehydes.[26] As relatively few examples of oxazoline synthesis via NHC–Au catalyzed processes have been reported in the literature, we were interested in testing multinuclear gold (I) complexes as precatalysts for the above-mentioned reaction. Thus, the catalytic performance of complexes 1–3 was tested in the cyclization of N-2(propyn-1-yl)benzamide to produce the corresponding oxazoline. The reactions were performed at room temperature with an initial complex loading of 3 mol% (based in the metal) and the addition of $AgBF_4$ (equal mol% based in the amount of gold contained in complexes 1–3) to render catalytically active cationic Au(I) species. As observed in Table 3, the initial conditions clearly demonstrate the enhanced performance of the dinuclear and trinuclear complexes com-

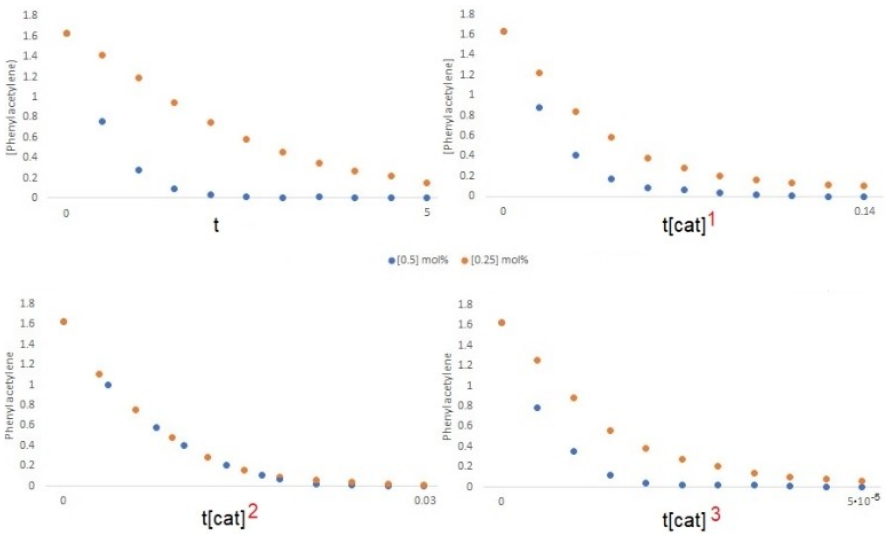
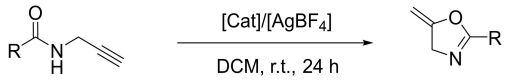


Figure 4. Determination of reaction order in catalyst 3 by the normalized scale method.[27]

Table 3. Synthesis of substituted oxazolines using MIC–Au complexes 1–3 as precatalysts.[a]



Entry	R	[Cat]	Conv [%][b] at 3[mol%] [Cat]	Conv [%][b] at 1[mol%] [Cat]
1	Ph	1	76	47
2	Ph	2	97	88
3	Ph	3	99	93
4	4-(Br)Ph	1	72	46
5	4-(Br)Ph	2	95	87
6	4-(Br)Ph	3	95	89
7	4-(OMe)Ph	1	68	49
8	4-(OMe)Ph	2	98	90
9	4-(OMe)Ph	3	98	94
10	n-hexyl	1	70	52
11	n-hexyl	2	90	83
12	n-hexyl	3	96	92

[a] Reaction conditions: *N*-propargyl amide (1.0 mmol), dichloromethane (3 mL), room temperature, catalyst and $AgBF_4$ (equal mol% based in the amount of gold contained in complexes 1–3). [b] Isolated yields as the average of two runs.

pared to the mononuclear analogue 1 (entries 1–3). Challenging the performance of the gold precatalysts by decreasing the complexes loading to 1 mol% (based in the metal) does not affect drastically the conversion percentages of 2 and 3; however, at 1 mol% loading, complex 1 decreases its conversion to a minimum of 47%. Furthermore, complexes 2 and 3 are highly successful in the cyclization of several propargylated amines rendering good to excellent yields with precatalyst 3 showing a slightly better performance. The catalytic performance of complexes 2 and 3 is comparable to the recently reported gold triazolylidene complexes.[26,27]

To gain deeper insight into the enhanced catalytic performance of complex 3, we sought to explore the reaction order with respect to the catalyst. Hence, we have performed a study on the hydroamination of phenylacetylene with aniline using different concentrations (0.5 mol% and 0.25 mol%) of catalyst 3 and with a starting concentration of phenylacetylene of 1.63 mmol. Following the normalized time scale method $t[cat]_T^n$ reported by Bures and coworkers,[28] the overall data is consistent with a second order reaction with respect to the catalyst (Figure 4). Although catalytic cooperativity in multimetallic metal complexes is very difficult to prove, and in most cases, the difference in the catalytic behavior between catalysts with a different number of metal centers is only due to subtle differences in the steric and/or electronic properties of the catalysts, or simply to their different thermal stabilities, the kinetic results of the catalyst order suggest that the presence of various metals in the same ligand exert a positive effect in the catalytic performance, suggesting an increased local concentration of active catalytic sites under homogeneous conditions.

Conclusions

In summary, we have reported the convenient synthesis of a series of mono to trinuclear gold(I) complexes bearing phenoxy-functionalized triazolylidenes. All new compounds have been properly characterized by NMR spectroscopy, elemental analysis and in the case of complexes 1 and 2 by x-ray diffraction. The catalytic performance of the new air and moisture stable triazolylidene complexes (1–3) was tested in the hydration and hydroamination of terminal alkynes and in the preparation of oxazolines by the cyclization of propargylic amines. In general, the catalytic trials established the enhanced catalytic performance of the di- and trinuclear complexes 2 and 3 compared with the mononuclear complex 1. The increased efficiency of complexes 2 and 3 suggest the possibility of cooperative effects in these multinuclear complexes provided by a higher concentration of catalytically active species. The reaction scope and catalytic processes described in the present study demonstrate the broad applicability of the new multinuclear gold complexes. Continuous efforts related to the exploration of the catalytic potential of complexes 1–3 is currently being explored in our laboratory.

Experimental Section

Commercially available reagents and solvents were used as received. Triazolium salts I–III were synthesized as reported in the literature.[10] Synthesis of all metal complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. NMR spectra were obtained with a Bruker Ascend (400 MHz) spectrometer. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 2014 and refined by full matrix least squares against F^2.[29] All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms was kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table 4.

Deposition Number 2042495 (for 1) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

General procedure for the synthesis of gold complexes 1–3

Complex 1. Chloro(dimethylsulfide)gold (34 mg, 0.114 mmol), potassium hexamethyl disylazide (30 mg, 0.149 mmol) and triazolium salt I (50 mg, 0.115 mmol) were combined in a Schlenk flask and dissolved in THF (9 mL) at −78 °C. The resulting mixture was stirred for 18 h while reaching room temperature. The final clear suspension was dried under vacuum and the residue was extracted with benzene (10 mL). After cannula filtration and removal of the solvent, the crude material was purified via chromatography

Table 4. Crystallographic Data and Summary of Data Collection and Structure Refinement.

	Complex 1
Formula	$C_{19}H_{21}AuIN_3O$
Fw	631.25
cryst syst	Triclinic
Space group	P-1
T, K	293(2)
a, Å	8.8041(9)
b, Å	11.1241(12)
c, Å	11.8001(10)
α, deg	112.284(9)
β, deg	90.660(7)
γ, deg	103.686(9)
V, Å^3	1032.39(19)
Z	2
d_{calc} g.cm^{-3}	2.031
μ, mm^{-1}	8.631
refl collected	8642
T_{min}/T_{max}	0.922
N_{measd}	4670
[R_{int}]	0.0711
$R[I > 2sigma(I)]$	0.0554
R (all data)	0.1033
$R_w[I > 2sigma(I)]$	0.0975
R_w (all data)	0.1307
GOF	1.043

column using a mixture of dicloromethane/ethanol (95:5) providing the title product as white solid in 63% yield (45 mg, 0.72 mmol). m.p. = 172–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.23 (m, 2H, CH_{ar}), 7.02–6.94 (m, 3H, CH_{ar}), 6.89 (s, 2H, CH_{mes}), 5.32 (s, 2H, CH_2), 4.22 (s, 3H, NCH_3), 2.27 (s, 3H, CH_3), 1.92 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2 (C–Au), 157.0 (C_{ar}), 142.0 (C_{tz}), 140.9 (C_{ar}), 135.2 (C_{ar}), 134.3 (C_{ar}), 129.9 (CH_{ar}), 129.5 (CH_{ar}), 122.4 (CH_{ar}), 115.1 (CH_{ar}), 60.1 (CH_2), 38.2 (NCH_3), 21.3 (CH_3), 17.9 (CH_3). Found: C, 36.42; H, 3.56; N, 6.39; Calc for: $C_{19}H_{21}AuIN_3O$ C, 36.15; H, 3.35; N, 6.66.

Complex 2. According to the general procedure but using chloro (dimethylsulfide)gold (37 mg, 0.126 mmol), potassium hexamethyl disylazide (33 mg, 0.164 mmol), and bis-triazolium salt (50 mg, 0.063 mmol), the title product was obtained as a white solid in 81% yield (60 mg, 0.051 mmol) after purification via chromatography column using a mixture of dicloromethane/ethanol (90:10). m.p. = 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (t, *J* = 8.2 Hz, 1H, CH_{ar}), 7.08 (t, *J* = 2.2 Hz, 1H, CH_{ar}), 6.96 (s, 4H, CH_{mes}), 6.69 (dd, *J* = 8.2, 2.3 Hz, 2H, CH_{ar}), 5.44 (s, 4H, CH_2), 4.33 (s, 6H, NCH_3), 2.32 (s, 6H, CH_3), 1.98 (s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1 (C–Au), 158.4 (C_{ar}), 141.7 (C_{tz}), 140.8 (C_{ar}), 135.1 (C_{ar}), 134.3 (C_{ar}), 130.7 (CH_{ar}), 129.5 (CH_{ar}), 109.7 (CH_{ar}), 101.8 (CH_{ar}), 60.3 (CH_2), 38.5 (NCH_3), 21.3 (CH_3), 17.9 (CH_3). Found: C, 35.11; H, 3.34; N, 7.00; Calc for: $C_{32}H_{36}Au_2I_2N_6O_2$ C, 32.45; H, 3.06; N, 7.10.

Complex 3. According to the general procedure but using chloro (dimethylsulfide)gold (38 mg, 0.130 mmol), potassium hexamethyl disylazide (33 mg, 0.167 mmol), and bis-triazolium salt (50 mg, 0.043 mmol), the title product was obtained as a white solid in 73% yield (54 mg, 0.031 mmol) after after purification via chromatography column using a mixture of dicloromethane/ethanol (90:10). m.p. = 214–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (s, 6H, CH_{mes}), 6.67 (s, 3H, CH_{ar}), 5.45 (s, 6H, CH_2), 4.36 (s, 9H, NCH_3), 2.34 (s, 9H, CH_3), 1.99 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1 (C–Au), 159.0 (C_{ar}), 141.5 (C_{tz}), 140.8 (C_{mes}), 135.1 (C_{mes}), 134.2 (C_{mes}), 129.4 (CH_{mes}), 96.7 (CH_{ar}), 60.1 (CH_2), 38.6 (NCH_3), 21.2 (CH_3), 17.9 (CH_3). Found: C, 31.82; H, 3.55; N, 6.98; Calc for: $C_{46}H_{54}Au_3I_3N_9O_3$ C, 31.52; H, 3.11; N, 7.19.

Catalytic procedure for the hydroamination of phenylacetylene using complexes 1–3

Typical procedure for catalytic hydroamination of alkynes: A Schlenk flask was charged with the proper catalyst/$AgSbF_6$ mixture [complex 1 (0.5 mol%)/$AgSbF_6$ (1.0 mol%); complex 2 (0.25 mol%)/$AgSbF_6$ (0.5 mol%) or complex 3 (0.167 mol%)/$AgSbF_6$ (0.334 mol%)] and evacuated and filled with nitrogen three times. Afterward, the corresponding arylamine (0.55 mmol), phenylacetylene (0.5 mmol) were subsequently added. The resulting mixture was stirred at 40 °C for 3 h. The final reaction mixture was filtered through celite and the supernatant concentrated under vacuum. The products were purified directly by column chromatography on silica gel using appropriate mixtures of petroleum ether/diethyl ether as eluent.

General procedure for the hydration of alkynes catalysed by complexes 1–3

To a 20 mL scintillation vial equipped with stirring bar was first added the corresponding alkyne (1.0 mmol) followed by MeOH (5 mL) and water (4.0 mmol). In the case of insoluble alkynes, CH_2Cl_2 (1 mL) can be added to improve solubility. Afterward, the proper catalyst/$AgSbF_6$ mixture [complex 1/$AgSbF_6$ (3 mol% each); complex 2/$AgSbF_6$ (1.5 mol% each); complex 3/$AgSbF_6$ (1.0 mol% each)] was added and the reaction mixture was stirred at 60 °C for 24 h. After the reaction was completed, the solvents were evaporated. The residue was dissolved in DCM (10 mL) and the resulting solution filtered over a short plug of silica, which was washed with DCM (5 mL). The combined filtrates were evaporated under reduced pressure to afford the respective ketone.

General procedure for the catalytic cyclization of propargylated amides using complexes 1–3

The proper catalyst/$AgBF_4$ mixture [complex 1/$AgBF_4$ (1 mol% each); complex 2/$AgBF_4$ (0.5 mol% each); complex 3/$AgBF_4$ (0.34 mol% each)] and 3 mL of dry dichloromethane were charged in a 5 ml screw capped scintillation vial. After the mixture was stirred 10 min, the proper propargylated amide was added (1.0 mmol) and the mixture stirred for 24 h at room temperature. The solvent was removed under vacuum and the residue was extracted with diethyl ether, washed with brine, and dried with Na_2SO_4. The organic layer was evaporated, and the crude product was purified by silica gel column using ethyl acetate/petroleum ether as eluent.

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Conflict of Interest

The authors declare no conflict of interest.

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