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Formal Insertion of a Metal Carbene Complex into a σ-Carbon-Carbon Bond. Gold-Catalyzed Synthesis of 3*H*-Indoles

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Abstract: We report here a formal insertion of a metal carbene complex in a single carbon-carbon bond. This behavior occurs with the participation of an α-imino gold carbene complex, generated from benzofused triazapentalenes or, in a one-pot procedure, from their 1-propargyl-1*H*-benzotriazole precursors, and gold-catalytically activated ynamides. As the result, 3*H*-indole derivatives were obtained, with formation of a quaternary center. A computational analysis carried out on the reaction mechanism indicates that the bulkiness of the gold ligand plays a key role forcing a conformation, which includes aromatic interactions, that favors the approximation of the carbenic carbon to the reactive site. In addition, a negative crossover experiment rules out a cationic arene migration pathway.

Keywords: Carbenes; Catalysis; Gold; Heterocycles; Insertion

The development of strategies using gold catalysis has led to a plethora of carbo and heterocycle forming processes over the last decades.[1] Among the different types of gold intermediates, gold carbene complexes have emerged as key intermediates for a large number of processes and their nature have been profusely studied.[2] In this sense, mechanistic proposals postulating the participation of metal carbene complexes as intermediates in different types of formal insertions, have been widely described. Although C–H insertions of metal carbene complexes are commonly described,[3] examples of other types of single bond formal insertions such as O–H,[4] S–H,[5] N–H,[6] P–H,[7] F–H,[8] Si–H,[9] or B-H[10] have also been mentioned. However, to the best of our knowledge, although few examples of carbon-heteroatom formal insertions have been reported,[11] apart from ring expansions or migratory insertions, no examples of a formal direct insertion of a metal carbene complex intermediate in a carbon-carbon σ-bond can be found to date.[12] A close result, reported by Zhu and coworkers,[13] implies a gold-catalyzed formal insertion of diazocompounds in 1,3-diketones (Figure 1, *top*), but the carbene complex reacts with the double bond of the enolic form, through a cyclopropanation, and not directly over a single bond. Similar behavior was reported by Bi group with silver complexes and diazocompounds[14] or nosylhydrazones.[15]

Moreover, benzofused triazapentalenes, or their corresponding 1-propargyl-1*H*-benzotriazole precursors, have emerged as valuable tools for heterocyclic synthesis,[16] involving the participation of α-imino gold carbene complexes as intermediates, in their reaction with gold-activated alkynes.[17] In Figure 1 (*midddle*) two examples of catalytic and atom economical indole skeleton formation involving a gold carbene participation in a C–H activation or an aza-Nazarov

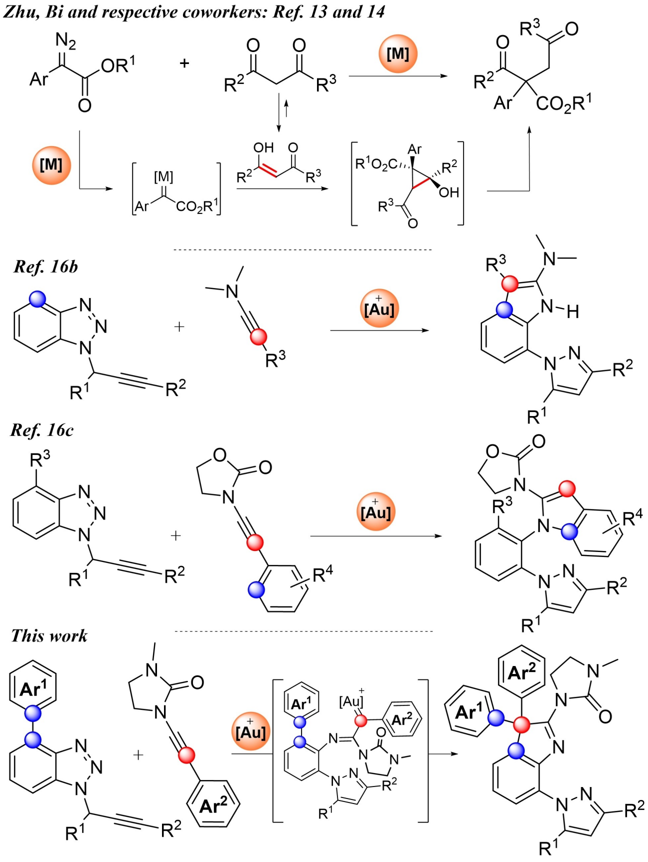
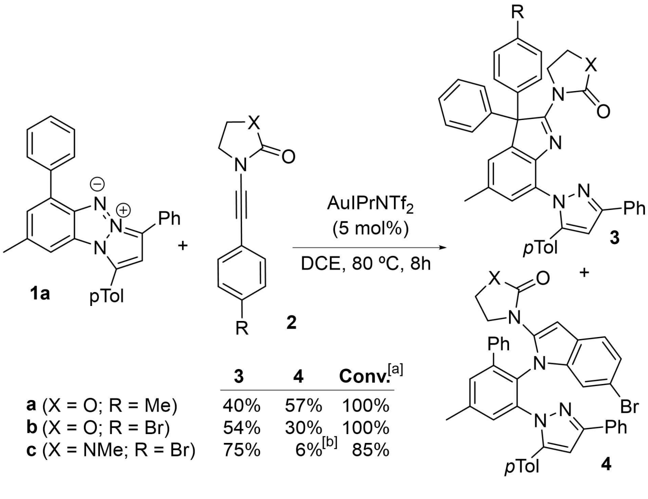


Figure 1. Related results and working hypothesis.



	3	4	Conv.[a]
a (X = O; R = Me)	40%	57%	100%
b (X = O; R = Br)	54%	30%	100%
c (X = NMe; R = Br)	75%	6%[b]	85%

Scheme 1. Preliminary results. Isolated yields for the formation of indole derivatives **3a–c** and **4a–b**. [a] Determined by NMR spectroscopy using dibromomethane as internal standard. [b] Not isolated. DCE = 1,2-dichloroetane.

reaction, respectively, are presented. Continuing with our efforts in the study of these systems, we observed that the presence of electron withdrawing groups at the ynamide arene ring favored the formation of a third indole family and, much more relevantly, involves an unprecedented formal insertion of the gold carbene intermediate in a single carbon-carbon bond (Figure1, *bottom*).

Herein we present the first formal carbon-carbon insertion of a metal carbene complex into a biarylic single bond. The procedure involves a gold-catalyzed and atom economical reaction of a triazapentalene derivative and an ynamide, yielding to the creation of an indole derivative bearing a quaternary carbon. The initial hypothesis for the reaction mechanism was supported by a computational study.

During the course of our investigations, we observed that benzofused triazapentalene **1a** reacted with ynamide **2a**, in 1,2-dichloroethane at 80 °C, in the presence of a 5 mol% of IPrAuNTf$_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene) yielding a 40% of the unexpected indolyl compound **3a** (Scheme 1). In addition, a 57% of previously reported[16c] indole **4a**, emerged from an aza-Nazarov reaction. Yield of compound **3** raised up to 75% (85% conversion) under the same reaction conditions, using ynamide **2c** bearing an electron-withdrawing group, and replacing the 2-oxazolidinone by a 2-imidazolidinone moiety. Both modifications greatly diminished the formation of the competitive aza-Nazarov product **4**.

The structure of indoles **3**, was unambiguously confirmed by a X-ray analysis of a crystal of compound **3b**,[18] obtained from a methylene chloride/hexane solution (Figure 2). From this structure, it can be deduced that the β-carbon of the ynamide -precursor of the carbene carbon (highlighted in red in Figure 1, *bottom*) - has been inserted between the two connected *ipso*-carbons of the arene rings of triazapentalene skeleton (in blue in Figure 1, bottom). Moreover, a quaternary center has been created.

At this point, we decided to perform several screening experiments in order to optimize the solvent and reaction conditions for the formation of compound **3c**. The best results were obtained performing the reaction in a 0.4 M solution of chloroform at 80 °C, in a sealed tube, during 18 h (see *Supporting Information*). More interestingly, every attempt to replace the

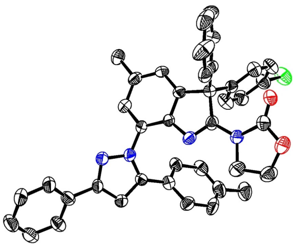
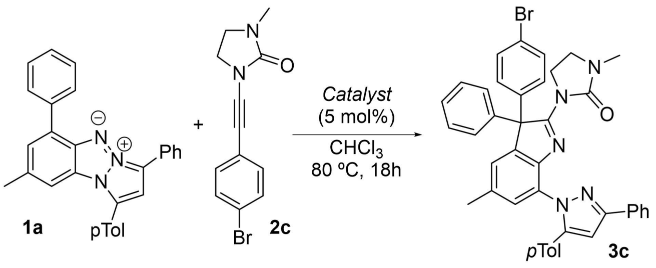


Figure 2. ORTEP view of indole **3b** with thermal ellipsoids at the 40% level. Hydrogen atoms omitted for clarity.

$IPrAuNTf_2$ catalyst by other gold species with different ligands, resulted in a dramatically decrease of the reaction yield (Scheme 2) suggesting that the nature of the 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene ligand exerts a decisive influence in the reaction course.

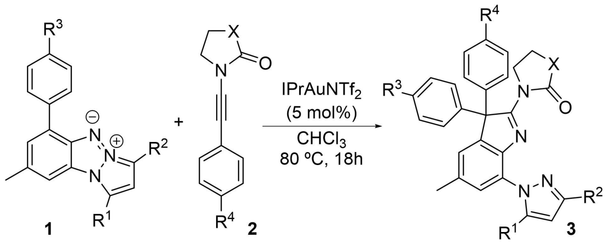


Catalyst	Yield: 3c	/ 4c	/ Conv.[a]
$IPrAuNTf_2$:	96%[b]	-	100%
$JohnPhosAuNTf_2$:	9%	-	35%
$Ph_3PAuCl/AgNTf_2$:	< 3%	-	30%
$(ArO)_3PAuNTf_2$:	< 3%	<3%	32%
$PicAuCl_2$:	18%	<3%	35%

Scheme 2. Gold catalyst ligand screening. [a] Yields and conversions determined by NMR spectroscopy using dibromomethane as internal standard.[b] Isolated yield.

Once the optimal reaction conditions were established, we explored the scope of the reaction in terms of the substitution patterns of triazapentalene **1** and ynamide **2** (Table 1). As it is shown in Table 1, the reaction perfectly tolerates the presence of electron-donating (compounds **3 d–e,q**) or electron-withdrawing groups (compound **3 f**) at the arene ring attached to the triazapentalene **1**, without a significant influence. However, the electronic nature or the arene ring of the ynamide **2** is more relevant due to the competition with the formation of indole **4**. Thus, the best results were obtained using ynamides with electron-withdrawing groups placed at that point. In this sense, the reaction tolerates the presence of several functional groups. However, the presence of strong electron-donating groups, such as a methoxy group (compound **3 n**), strongly deflects the reaction course towards the major formation of indole **4 n**. This effect is in

Table 1. Reaction scope.



Compound	R^1	R^2	R^3	R^4	X	Yield [%][a]
3 b	*p*Tol	Ph	H	Br	O	64[b]
3 c	*p*Tol	Ph	H	Br	NMe	96
3 d	*p*Tol	Ph	Me	Br	NMe	89
3 e	*p*Tol	Ph	OMe	Br	NMe	88
3 f	*p*Tol	Ph	F	Br	NMe	80
3 g	*p*Tol	Ph	H	F	NMe	81
3 h	*p*Tol	Ph	H	CO_2Me	NMe	73
3 i	*p*Tol	Ph	H	CN	NMe	49
3 j	*p*Tol	Ph	H	CF_3	NMe	76
3 k	*p*Tol	Ph	H	Ph	NMe	83
3 l	*p*Tol	Ph	H	H	NMe	68[c]
3 m	*p*Tol	Ph	H	Me	NMe	74[d]
3 n	*p*Tol	Ph	H	OMe	NMe	12[e]
3 o	Ph	Ph	H	Br	NMe	81
3 p	Ph	*p*Tol	H	Br	NMe	91
3 q	Ph	*p*Tol	Me	Br	NMe	82
3 r	PMP	Ph	H	Br	NMe	73
3 s	*p*Tol	Ph	H	Br	NPh	87

[a] Isolated yields.
[b] 25% yield of **4 b**.
[c] 81% of conversion.
[d] 24% yield of **4 m** (not isolated).
[e] 74% yield of **4 n**.

agreement with the previously reported formation of *N*-aryl indoles **4** from a gold-catalyzed reaction of benzotriazole derivatives and electron-rich ynamides[16c] through a mechanism that involves an aza-Nazarov cyclization of the carbene intermediate. Finally, the reaction could also be performed with ynamides bearing an *N*-aryl urea (compound **3 s**).

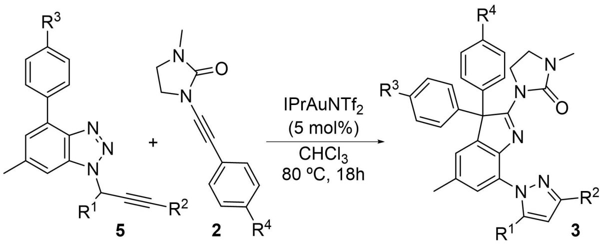
These processes represent a high yielding and atom economical gold-catalyzed methodology for the synthesis of indole derivatives, with formation of a quaternary center. This quaternary center results from the migration of an arene ring from the triazapentalene to the C3 of the indole ring. More relevantly, the β-carbon of the ynamide has been inserted into the single carbon-carbon that joins the two arene rings. Since that ynamide carbon gives rise to the gold carbene carbon of the α-imino gold carbene intermediate, the reaction mechanism involves an insertion of a metal carbene complex in a single carbon-carbon bond, later supported by a computational study (*vide infra*).

As the next step, formation of compounds **3** can also be achieved starting from propargyl-1*H*-benzotriazole precursors[16a] of the triazapentalenes **1**, in a one-pot procedure. For that purpose, benzotriazole **5** was initially[19] stirred in chloroform at 50 °C for three hours in the presence of the gold catalyst (IPrAuNTf$_2$). Thus, after addition of the corresponding ynamide **2** to the reaction vessel and 18 hours of stirring, under the standard reaction conditions, indoles **3** were obtained and the results are reported in Table 2. From this table, it can be inferred that the reaction operates satisfactorily with only a slight decrease of the reaction yield, compared to the process starting from benzofused triazapentalenes **1**.

Once the scope of the reaction was stablished, we focused our efforts towards the unraveling of the reaction mechanism. Thus, as the structure on indoles implies a migration of the arene ring from the benzotriazole skeleton to the C3 of the indole ring, we initially performed a crossover experiment in order to elucidate if the arene migration could involve or not a free arenium cation, through an outer sphere migration, probably assisted by the triflimidate counterion. However, when a mixture of triazapentalenes **1 b** and **1 f** was reacted with ynamide **2 c**, under the standard reaction conditions, only two indole derivatives (**3 d** and **3 p**) were observed, without formation of any amount of indoles **3 c** or **3 q** (Scheme 3). The absence of exchange between the respective arene rings indicates that those arene rings do not migrate as independent cationic areniums.

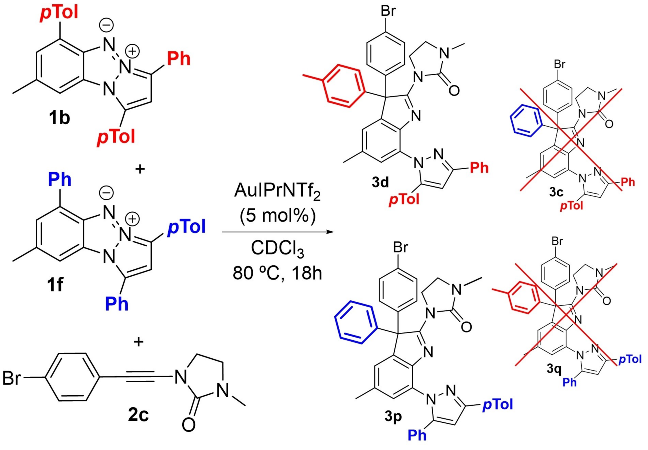
Our next step was to perform a complete computational study on the reaction mechanism under the framework of the density functional theory (DFT). We used the M06 functional[20] and the SDD (ECP) basis set[21] for Au and 6–31 + G(d,p)[22] for the rest of the atoms, following the good results already obtained using this methodology for similar reactions[23] (see Supporting Information for details). The solvent effect was considered through the SMD implicit solvent model (dichloroethane as the solvent) in the optimization and the frequency calculations.[24] The complete structures of **1**, **2** and the gold catalyst were considered. As we will discuss below, this is crucial for the

Table 2. Synthesis of indole derivatives **3** from propargyl-1*H*-benzotriazoles **5**.



Compound	R^1	R^2	R^3	R^4	Yield [%][a]
3 c	*p*Tol	Ph	H	Br	81
3 d	*p*Tol	Ph	Me	Br	77
3 e	*p*Tol	Ph	OMe	Br	75
3 f	*p*Tol	Ph	F	Br	79
3 g	*p*Tol	Ph	H	F	80
3 h	*p*Tol	Ph	H	CO_2Me	47
3 j	*p*Tol	Ph	H	CF_3	70
3 k	*p*Tol	Ph	H	Ph	71
3 m	*p*Tol	Ph	H	Me	60
3 p	Ph	*p*Tol	H	Br	84

[a] Isolated yields.



Scheme 3. Negative crossover experiment.

adequate mechanism exploration. Figure 3 illustrates the computed reaction mechanism.

The previous reaction steps starting from **1** and **2** and leading to the formation of **I** are omitted for clarity (see *Supporting Information*). The interaction between the species in **I** includes stabilizing aromatic interactions[25] involving the Au ligand, the alkyne substituent and the benzofused triazapentalene. The two species in **I** then interact through a nucleophilic attack to yield **II**, slightly more stable, through a small energy barrier (**TS-I**, 11 kcal/mol). The N–N bond is then broken through a small energy barrier (**TS-II**, 6.9 kcal/mol) leading to the relatively stable gold carbene intermediate **III**. Interestingly, the high steric demand of the gold coordination sphere, due to the volume of the IPr ligand,causes a geometric disposition in which the bromo and phenyl-substituted aromatic rings have an almost parallel arrangement. Both aromatic rings approach to each other (C–C distances ranging from 3.2 to 3.8 Å) which probably contributes to stabilization due to aromatic interaction. In addition, this geometry in **III** also place the carbenic carbon and the phenyl-substituted *ipso* atom at 3.353 Å. These two atoms further approach in **TS-III** (at 2.191 Å) with an energy barrier of 17.7 kcal/mol. Again, the gold moiety contributes to block the geometry of this transition

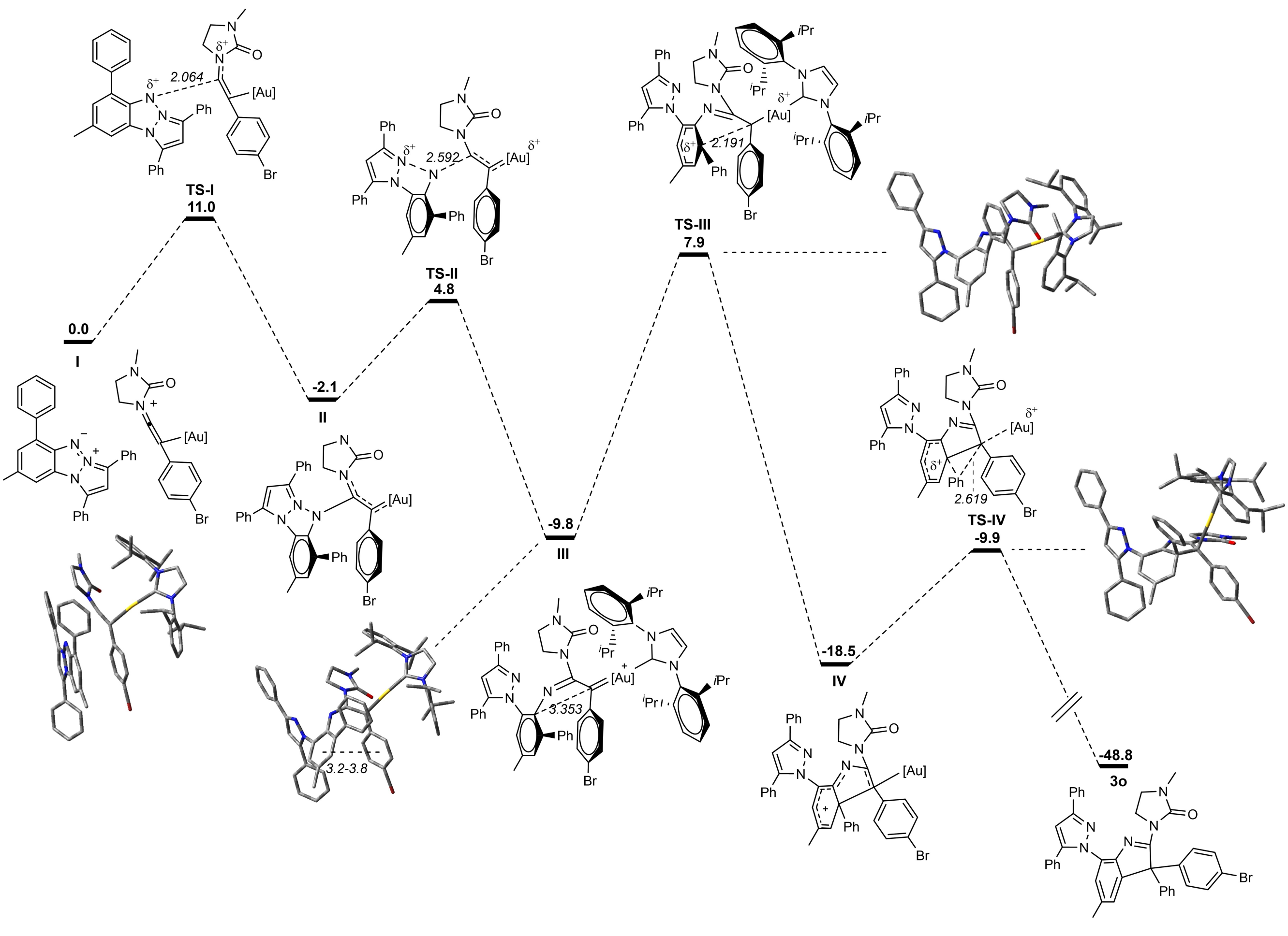


Figure 3. Computed reaction mechanism for the formation of **3 o**. Relevant geometries discussed in the text are shown. Hydrogen atoms omitted for clarity. Distances in angstroms. Free energies in kcal/mol relative to **I**.

state, and allows for the interaction of the phenyl rings while the interacting parts of the molecule approach. This is in agreement with the experimental observations shown in Table 2, in which other gold catalysts imply poor conversion. A very stable intermediate **IV** is then formed in which the indole cyclic moiety is already present although substitution prevents aromatization. Thus, the next reaction step implies a phenyl rearrangement, which allows for indole aromatization. As supported by the negative crossover experiment, this does not imply a free arenium rearrangement. In agreement with this experiment, computational data revealed an early transition state for the Ph migration. In **TS-IV**, Ph starts to migrate (Ph-$C_{initial}$-C_{final} angle goes from 115° to 114°). The $C_{initial}$-Ph distance elongates (1.562 Å *vs.* 1.565 Å) and C_{final}-Ph shortens (2.628 Å *vs.* 2.619 Å). At the same time, the organic core adapts: planarization of the initial ring leading to aromatization (from 28.6° to 27.3°) and the C–C bond in the five member transforms from a partially double bond to the single bond in the final product (1.438 Å to 1.445 Å). The driving force for this step is the stabilization obtained in the final product. Overall, the reaction mechanism implies a series of steps guided by the increase in thermodynamic stability with accessible energy barriers under the reaction conditions. It is clear the critical role of the catalyst ligands to explain the observed outcome. Moreover, the presence of **III** and **IV** as very stable intermediates could allow for divergent reaction pathways.

In summary, we report here a simple, high yielding and atom economical gold catalyzed synthesis of 3*H*-indole derivatives through the participation of α-imino gold carbene complexes, as intermediates. As the main breakthrough, this work describes, for the first time, a formal insertion of a metal carbene intermediate in a single biarylic carbon-carbon bond. For that purpose, the α-imino gold carbene complex was catalytically generated using benzofused triazapentalene derivatives as starting material, giving rise to the indole derivative in their reaction with ynamides. Moreover, similar results were obtained starting from 1-propargyl-1*H*-bentrotriazoles, in a one-pot procedure, without significant changes. A computational study performed on the reaction mechanism revealed, in the gold carbene intermediate, an oncoming of the carbene carbon to a reactive nucleophilic position forced by the key influence exerted by the IPr (1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene) gold ligand, together with a cooperative aromatic interaction between arene rings. These studies, in addition to a crossover experiment, give support to the mechanistic proposal. Finally, 3*H*-indole derivatives obtained as reaction products incorporate the formation of a quaternary center.

Experimental Procedure for the Synthesis of 1*H*-pyrazol-1-yl-3*H*-indoles 3

From Benzofused triazapentalenes 1

In a sealed tube, under argon atmosphere, a solution, in 0.5 mL of chloroform, of 0.2 mmol of benzofused triazapentalene **1**, 0.3 mmol of the corresponding inamide **2** and 0.01 mmol (8.7 mg, 5 mol%) of the gold(I) catalyst ($IPrAuNTf_2$), is prepared. The mixture was stirred for 18 h at 80 °C. After that period, the solvent was removed under vacuo and the residue was purified through a chromatographic column, to obtain pure indoles derivatives **3**.

*From 1-propargyl-1*H*-bentriazoles 5*

In a sealed tube, under argon atmosphere, a solution, in 0.25 mL of chloroform, of 0.2 mmol of 1-propargyl-1*H*-bentriazole **5**, and 0.01 mmol (8.7 mg, 5 mol%) of the gold(I) catalyst ($IPrAuNTf_2$), is prepared. The mixture was heated to 50 °C and stirred for 2 hours. Next, a solution of 0.3 mmol of the corresponding inamide **2** in 0.25 mL of chloroform was added via syringe. The mixture was heated to 80 °C following to the end the same procedure describe starting from benzofused triazapentalene **1**.

Experimental SectionAcknowledgements

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