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Gold(III) Auracycles

Gold(III) Auracycles Featuring C(sp^3)-Au-C(sp^2) Bonds: Synthesis and Mechanistic Insights into the Cycloauration Step

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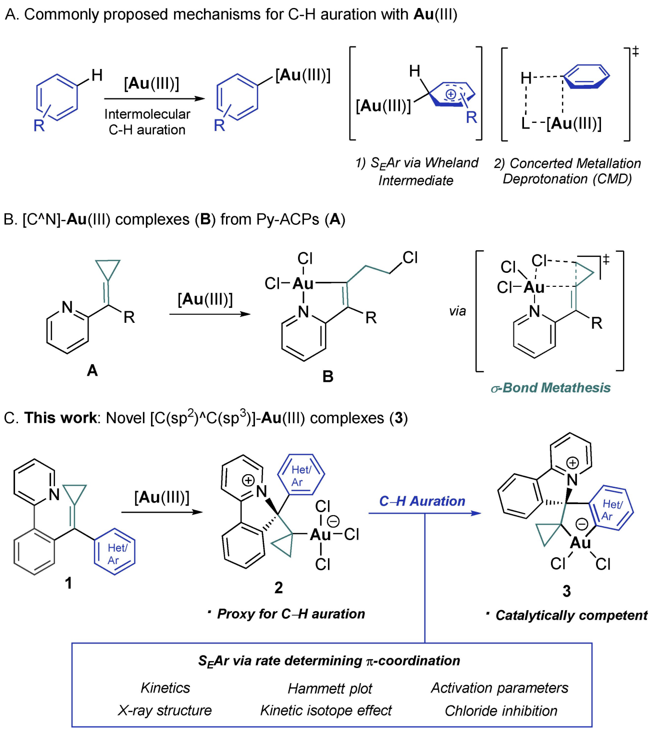
Abstract: The direct auration of arenes is a key step in numerous gold-catalyzed reactions. Although reported more than 100 years ago, understanding of its underlying mechanism has been hampered by the difficulties in the isolation of relevant intermediates given the propensity of gold(III) species to undergo reductive elimination. Here, we report the synthesis and isolation of a new family of intriguing zwitterionic [C(sp^3)^C(sp^2)]-auracyclopentanes, as well as of their alkyl-gold(III) precursors and demonstrate their value as mechanistic probes to study the C(sp^2)-Au bond-forming event. Experimental investigations employing Kinetic Isotope Effects (KIE), Hammett plot, and Eyring analysis provided important insights into the formation of the auracycle. The data suggest a S$_E$Ar mechanism wherein the slowest step might be the π-coordination between the arene and the gold(III) center, en route to the Wheland intermediate. We also show that these auracyclopentanes can work as catalysts in several gold-promoted transformations.

Introduction

The reaction of arenes with electrophilic gold(III) species to give aryl-gold(III) intermediates (i.e. direct arene auration) is a key step in a number of gold-catalyzed reactions, including synthetically appealing oxidative couplings that forge C(sp^2)-C or C(sp^2)-X bonds.[1–5] Interestingly, even if the direct auration of benzene has been known for almost one century,[6] in-depth understanding of this step is still very limited. "Standard" S$_E$Ar pathways, especially when electron-rich aromatic systems are involved, have been frequently invoked despite the lack of clear experimental evidence.[7] Alternatively, concerted metalation-deprotonation (CMD) processes have also been occasionally proposed (Scheme 1A).[8] Overall, this paucity of mechanistic studies sharply contrasts with the vast body of information gathered for oxidative couplings promoted by alternative metals, like Pd and Rh.[9]



Scheme 1. A. C–H auration in gold(III). B. [C^N]-Au(III) complexes (**B**) from Py-ACPs (**A**). C. This work: Intramolecular C–H arylation. Novel [C^C]-Au(III) carbophilic catalysts.

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A deeper understanding of this fundamental gold-mediated process is hampered by the difficulties in isolating representative arylgold(III) species given their high tendency to reductive eliminate compared to complexes of other transition metals.[10] Several cyclometalated gold(III) species based on bi- an tridentate ligands (e.g. [C^N], [P^C], [C^N^C], [N^C^C], etc.) have been prepared; however, their utility for studying elementary steps in gold catalyzed transformations is relatively limited.[11,12] Alternative auracycles featuring C–Au–C bonds might be much more relevant, but their synthesis and isolation are truly challenging.[13]

As a result of our interest in both gold catalysis and the chemistry of alkylidenecyclopropanes (ACPs),[14] our groups recently discovered that pyridine-substituted ACPs (**A**) readily react with gold(III) salts to deliver cyclometalated [C^N]-gold(III) complexes of type **B**, in a process that entails the opening of the cyclopropyl ring via a concerted σ-bond metathesis (Scheme 1B).[15] We have now found that separating the pyridine moiety from the ACP with an 1,2-phenyl tether (**1**, Scheme 1C) we can induce a completely different reactivity that results in the formation of intriguing carboauracycles of type **3**, featuring C(sp^2)-Au-C(sp^3) bonds. These products, which preserve the cyclopropyl ring, are formed through an unconventional cascade process entailing an alkene pyridine addition and an intramolecular C(sp^2)-H auration. Importantly, by controlling the reaction temperature, we could also isolate alkyl gold(III) species **2**, which precede the cyclometalation step, thus paving the way for an in-depth mechanistic investigation of the arene C–H auration process (Scheme 1C). The collected data allowed us to propose a S_EAr pathway in which a rate limiting gold(III)-arene complexation might precede the formation of the Wheland intermediate. Importantly, we also showcase the versatility of the alkene addition/auration cascade for a diverse range of precursors featuring aromatic or heteroaromatic rings and demonstrate that the resulting auracycles hold a promising profile as carbophilic gold catalysts.

Results and Discussion

Our studies commenced with the ACP **1a**, which bears a phenyl ring as connector between the alkene and the *ortho*-pyridine moiety. After initial exploratory experiments with different gold(III) sources,[16] we found that treatment of this compound with slight excess of sodium tetrachloroaurate in an MeCN/H_2O (1:1 v/v) mixture at 40 °C for 3 h, produces the zwitterionic cyclometalated-dichloroaurate **3a** in 45 % yield (Scheme 2A), whose unusual structure, with a spirocyclic moiety directly connected to gold(III), could be confirmed by X-ray analysis (vide infra).[16,17]

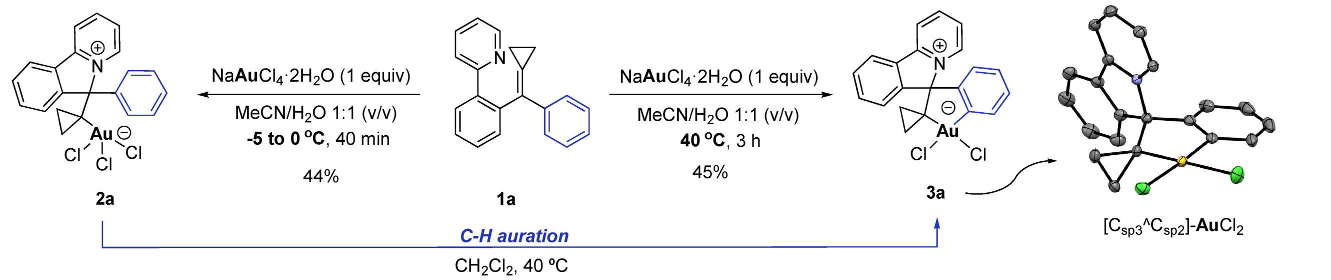
When the same reaction was performed at lower temperature, we observed a different gold complex, which could be identified by NMR and ESI-MS as the alkyl gold(III) species **2a**. Importantly, heating a solution of **2a** in CH_2Cl_2 promoted a mild conversion to the auracycle **3a**, which confirmed the direct connection between both complexes. The structures of these new gold(III) complexes captured our attention not only due to their unusual stability but also because of the limited amount of related zwitterionic gold(III) species,[18] particularly those involving carboauracyclic systems.[19] Also importantly, carboauracycles fearing a C(sp^3)–Au bond are very rare, and the few reported so far require a highly donating ancillary ligand at gold to warrant their stability (e.g. a phosphine or a NHC).[20]

Next, we explored the scope of the methodology for other substrates, such as **1b**–**1f**, equipped with different substituents at the phenyl moiety. Using the standard conditions from −5 to 0 °C, we obtained the expected alkyl gold species (**2**), except for precursor **1f**, which directly evolved to **3f** (Scheme 2B). Under the same conditions, but upon heating at 40 °C, we could obtain the auracycles **3**, except for **1c**, for which higher temperatures were needed to transform **2c** into **3c**. All the isolated complexes were stable, regardless the nature of the aromatic ring, and several single crystals could be obtained, either after interrupting the mechanical stirring at room temperature or by vapor diffusion.[16] A comparison between the structure of the auracycle **3c** and its acyclic precursor **2c** confirmed the spirocyclic moiety directly connected to the gold(III) center, which features a distorted square-planar geometry in both cases (Scheme 2C). The Au1–Cl2 bond length in **2c** is larger than the Au1–Cl1 and Au–Cl3 counterparts, likely as a result of a stronger *trans* influence of the carbon-based (C1) ligand. Thus, chloride Cl2 should be the most labile ligand in **2c**. Notably, metalacycle **3c** holds a larger bond length between nitrogen (N1) and the benzylic carbon (C7) than the acyclic precursor **2c** (1.532 Å and 1.518 Å, respectively).[21] This aligns well with a higher cationic character of C7 in **3c** than in **2c**. This distinct cationic character is also in agreement with the signals assigned to these benzylic carbon atoms (C7) in their corresponding ^{13}C NMR spectra (chemical shifts of 97.3 ppm for **3c** and 88.6 ppm for **2c**).[22]

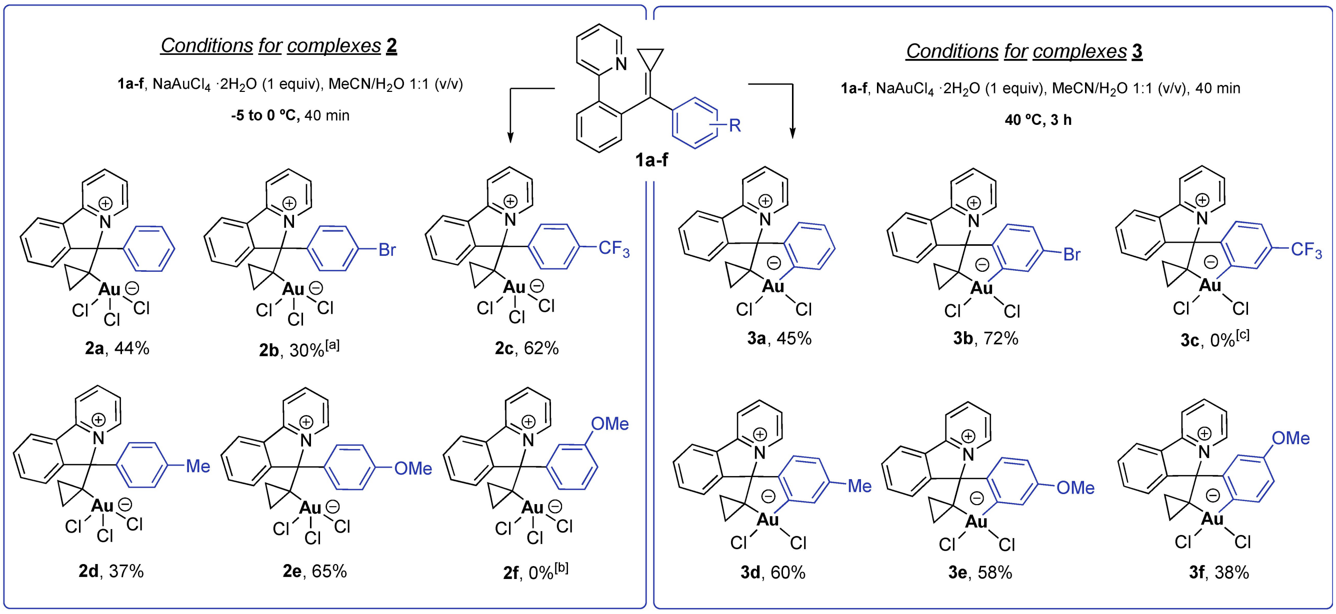
The cascade bicyclization process could be extended to different type of substrates, such as thiophene-substituted **1g**, which delivered the C2-auracyclic product **3g** at room temperature, in line with the higher reactivity observed also for the *p*-OMe-phenyl derivative **1f** (Scheme 2D).[23] Likewise, substrate **1h**, equipped with a 1-naphthyl moiety gave the auracycle **3h** in 57 % yield under ambient conditions. The alternative six-membered auracycle, putatively arising from the auration at the naphthalene C(8) position, was not observed. Replacing the pyridine nucleophile with a quinoline moiety (**1i**) resulted in acyclic product **2i** when the reaction was carried out at room temperature (48 % yield). Heating **1i** at 65 °C for 16 h delivered the auracycle **3i** in 45 % yield. Interestingly, a precursor lacking the cyclopropyl moiety (**1j**), delivered exclusively acyclic Au(III) complex **2j** in a 39 % yield at 40 °C. The cycloauration product **3j** could only be detected after prolonged heating of **2j** in DMSO at 120 °C. This result highlights the importance of the Thorpe–Ingold effect imposed by the cyclopropyl ring for the auration step.

The versatility of the methodology and the feasibility of isolating both, the auracycles **3** and alkyl-gold(III) precursors **2**, suggested that these complexes could be invaluable

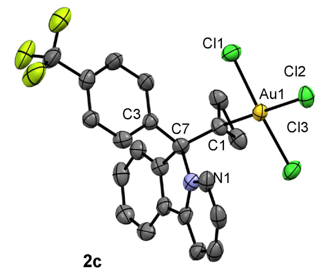
A. Isolation of Au(III) complexes **2a** and **3a** from Py-ACP **1a**



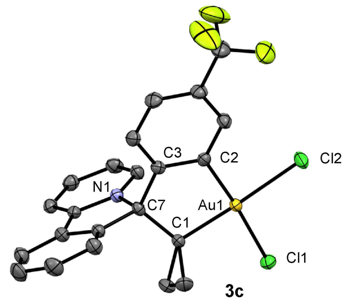
B. Synthesis of Au(III) complexes **2a-f** and **3a-f** with diverse substituents at the aromatic ring of the ACP



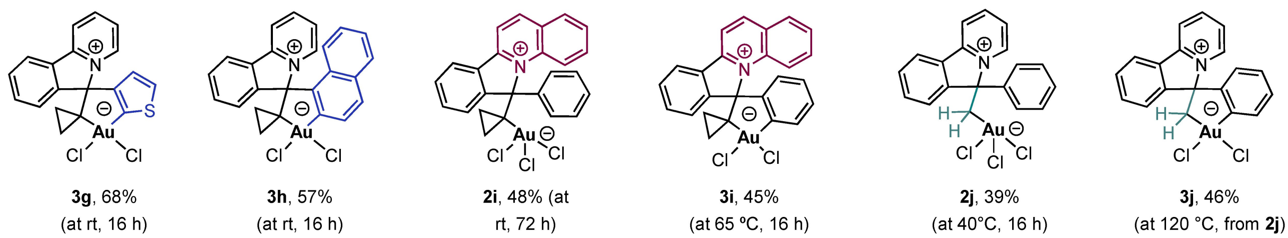
C. X-ray structure of **2c**, **3c** and table summarizing the relevant bond distances and angles[d]



Distance (Å) and Angle (°)		
Bond	2c	3c
Au1-Cl1	2.265 (2)	2.3592 (7)
Au1-Cl2	2.382 (2)	2.3655 (7)
Au1-Cl3	2.295 (2)	-
Au1-C1	2.078 (8)	2.043 (2)
Au1-C2	-	2.009 (2)
N1-C7	1.518 (9)	1.532 (3)
C1-C7-C3	118.2	107.6



D. Structural variations of the gold(III) complexes **2** and **3**[e]

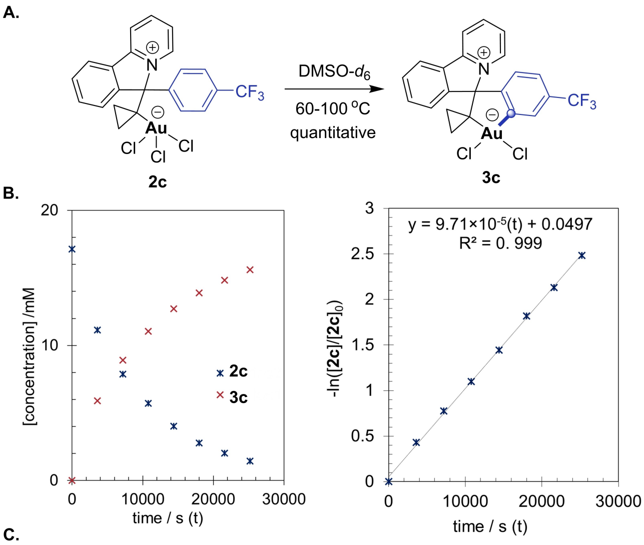


Scheme 2. [a] Reaction conducted in THF/H_2O (1:1 v/v).[b] Only product **3f** was obtained.[c] Product **3c** can be obtained heating **2c** at 100 °C in DMSO-d_6. [d] X-ray structure of **2c** and **3c** with ellipsoid at 50% probability (hydrogen atoms omitted for clarity) and table summarizing the relevant bond lengths (Å) and angles (°). [e] Reactions conducted in MeCN/H_2O (1:1 v/v) at 25 °C using [$NaAuCl_4$]·$2H_2O$ as gold(III) precursor.[17]

mechanistic probes for studying the C–H arene auration process. To this end, complex **2c** was dissolved in DMSO-d_6, along with ethylene carbonate as internal standard, and the solution heated at 100 °C and tracked by ^{1}H NMR spectroscopy. We observed a clean and almost quantitative conversion of **2c** to **3c** after 10 h (Scheme 3A).[16] In addition, concentrations of both species were calculated and plotted against time (Scheme 3B). The consumption of **2c** follows a clean first-order decay, $k = 9.42\times10^{-5}\ s^{-1}$, and the kinetics of the cyclometalation were reproducible, as showed by the standard deviation from three independent measurements ($2.57\times10^{-6}\ s^{-1}$).[16] When the reaction was carried out in the presence of increasing amounts of an exogenous chloride source (NBu_4Cl), the rate of the cyclometalation was attenuated and saturation kinetics were observed when $[NBu_4Cl]_0 = 2[\mathbf{2c}]_0$ ($k_{obs} = 4.86\times10^{-5}\ s^{-1}$).[16] These results suggest that a reversible dissociation of Cl^-, either precedes or is the rate-determining step. The activation parameters for the cycloauration of **2c** between 60 and 100 °C were calculated to be $\Delta H^{\ddagger} = 21.2$ kcal/mol and $\Delta S^{\ddagger} = -21$ e.u. (Scheme 3C).[16] The negative value of $\Delta S^{\ddagger}$ is consistent with a rate-determining transition state involving a system with less degrees of freedom compared to the precursor **2c**, rather than the chloride dissociation.[24]

The high reproducibility of the cyclometalation kinetics further confirmed that these compounds constitute an excellent platform to study the mechanism of arene auration. Thus, the first-order rate constants (k) for cyclometalation were measured at 60 °C for the five complexes (**2a–e**). A Hammett plot was devised using the rate constant of **2a** (k_H) as a reference to calculate $k_{rel} = k_x/k_H$ and the Hammett sigma value for *meta* substitution (σ^m),[25] disclosed in Scheme 4. A good correlation ($R^2 = 0.98$) was obtained for the cyclometalation reaction across four different complexes with a $\rho = -2.6$. This clearly indicates that the reaction is sensitive to electronic effects, and electron-rich substituents favor the cyclometalation over the electron-deficient counterparts.

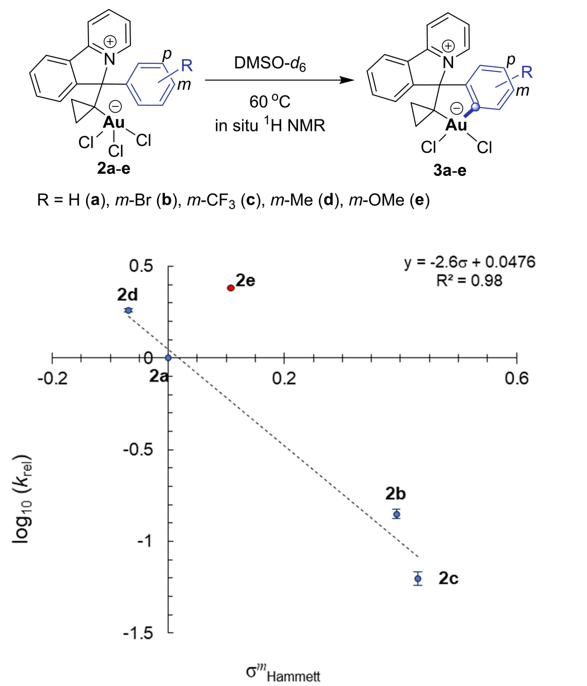
However, the experimentally obtained ρ value is significantly lower compared to those reported for S_EAr-like mechanisms where a direct formation of the Wheland intermediate is rate-limiting and typically feature ρ values lower than −3.5.[26] Further, it is worth mentioning that the cyclometalation of **2e** is not only the fastest among the analogous complexes, but also it is an outlier of the trend in the Hammett plot. While a change in the reaction mechanism for **2e** could justify this discrepancy, and cannot be fully discarded, a more likely explanation is that the transition state leading to Wheland intermediate is not rate determining, as otherwise a slower cyclometalation rate for **2e** should be observed compared to **2a**.



C.

Summary of kinetics			
Entry	$[\mathbf{2c}]_0$ / mM	Temperature / °C	Rate constant / s^{-1}
1	20	100	$9.42\times10^{-5} \pm 2.57\times10^{-6}$
2	20	90	$3.95\times10^{-5} \pm 4.05\times10^{-6}$
3	20	80	$2.29\times10^{-5} \pm 1.09\times10^{-6}$
4	20	70	$5.67\times10^{-6} \pm 1.53\times10^{-7}$
5	20	60	$2.96\times10^{-6} \pm 2.16\times10^{-7}$
6	20 [a]	100	4.86×10^{-5} [b]

Scheme 3. Cyclometalation of **2c** in DMSO-d_6. **A**. Representative example at 100 °C. **B**. Temporal concentrations of **2c** and **3c** and first-order plot for decay of **2c**, equations display the first-order decay (k) and correlation factor (R^2). **C**. Table summarizing the mean of three independent experiments and their standard deviation, calculated $\Delta H^{\ddagger} = 21.2$ kcal/mol and $\Delta S^{\ddagger} = -21$ e.u.[16] [a] Single experiment measured, reaction in presence of $[NBu_4Cl]_0 = 40$ mM. [b] Rate constant obtained using ^{19}F NMR.

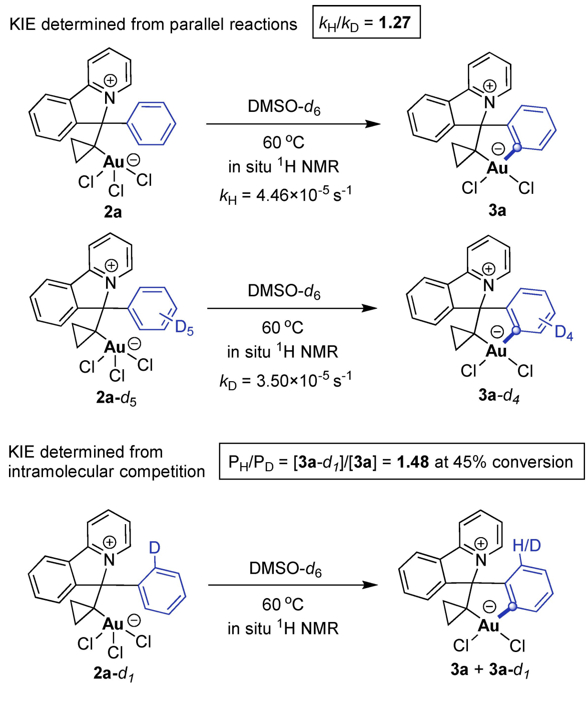


Scheme 4. Hammett plot of cyclometalation of acyclic gold(III) complexes **2a–e** in DMSO-d_6 at 60 °C. Linear correlation was calculated excluding **2e**. Equations display the $\rho = -2.6$ and correlation factor (R^2).

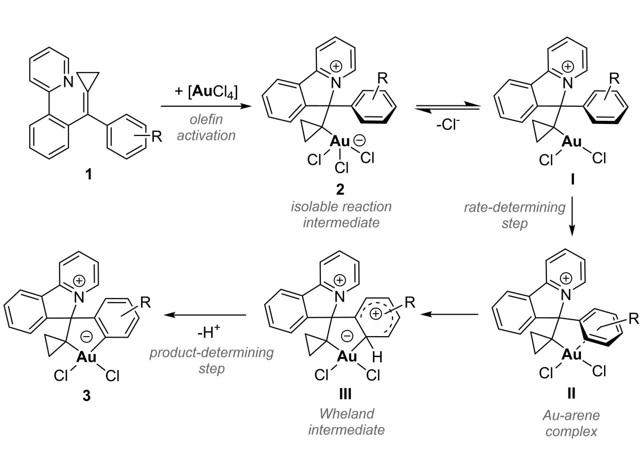
Kinetic isotope effects (KIE) were determined next using three different isotopologues: **2a**, **2a**-d_5 and **2a**-d_1, as depicted in Scheme 5. Firstly, the pseudo-first order decay (k_D) of the cyclometalation of **2a**-d_5 was obtained ($3.50\times10^{-5}\pm1.1\times10^{-6}$ s^{-1}) from three independent measurements at 60 °C, whereas the corresponding rate constant for **2a** (k_H) was calculated to be $4.47\times10^{-5}\pm1.1\times10^{-6}$ s^{-1} (KIE = 1.27).[27] The lack of a primary KIE clearly rules out the C–H bond cleavage as the rate-determining step. Further confirmation was obtained from the intramolecular competition in **2a**-d_1 to deliver **3a**-d_1 + **3a** as a mixture of isotopologues, giving a KIE = 1.48 showing that the reaction is irreversible and confirming that the C–H or C–D bond cleavage is product- but not rate-determining step in this process.[28]

Taken together, these experimental results are neither compatible with a classical S_EAr process nor with a CMD-mechanism, as neither the cleavage of the C–H bond nor the putative formation of a Wheland intermediate appear to be rate-limiting.[12o] We thus questioned whether some additional, less obvious interaction between the arene and the gold(III) could indeed be involved in the arene auration. Among the different options, the potential π-coordination to gold has been proved to be a key step in some gold-catalyzed arene couplings.[29] Detailed mechanistic investigations reported by Lloyd-Jones on the gold-catalyzed arylation of arenes have suggested that formation of a gold(III)-π-complex can be turnover limiting.[2b,d] The generation of such π complex resembled an associative process, where the rate is first-order in arene, with a negative rho value (ρ = −1.8) and large negative entropy of activation, which is in line with our experimental results.[2c] While the auration process in these previous studies could not be specifically investigated because the required intermediates were not isolated, our reaction system did allow the isolation of meaningful gold complexes providing additional experimental data. Therefore, we propose that the formation of the cycloaurated products starts by initial activation of the double bond in **1** by gold(III) followed by stabilization of the corresponding carbocation by the pyridine unit to afford intermediate **2**. Release of a chloride ion from gold generates a vacant site on the metal center, resulting in coordinatively unsaturated species **I**. The formation of a gold(III)-arene complex **II** might then be the rate-determining step. Finally, a S_EAr takes place, leading to the Wheland intermediate **III**, which evolves to metalacycle **3** through an irreversible C–H bond cleavage, as depicted in Scheme 6. Several attempts were made to detect species of type **I** or **II** by addition of chloride scavengers (e.g. AgX), using **2c** and a sterically demanding analog (**2k**) that could hamper the final cyclometallation (see SI). In all cases we just observed either the cyclometallated adduct (**3**) or gold(III) species related to **2**, in which the Au–Cl bond *trans* to the cyclopropyl carbon has been significantly labilized. While intermediates **I** or **II** were not detected, these results are compatible with the above proposal.[16]

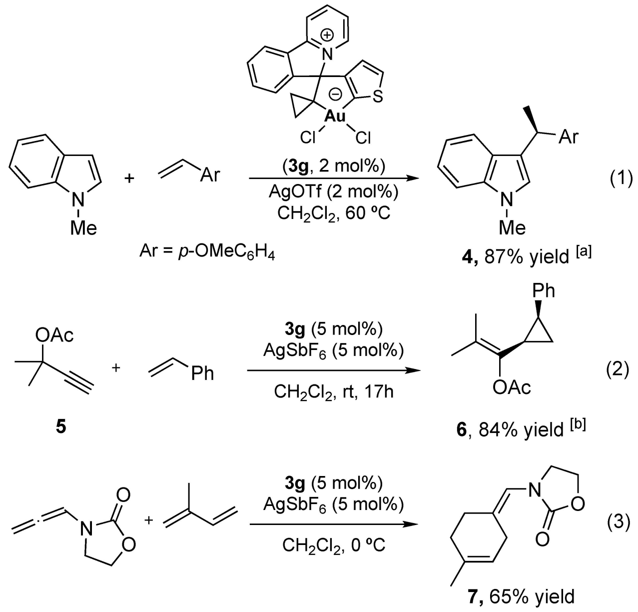
Finally, given the stability of most of these [C^C]-gold(III) complexes, and the lack of precedents on the use of auracyclopentanes in catalysis,[30,11d] particularly of those involving C(sp^3)-Au bonds, we made a preliminary exploration of their catalytic behavior. We first tested a hydroarylation process using styrene and *N*-methyl-indole as reactants (Scheme 7, eq 1).[31] We were glad to see that, upon chloride abstraction with equimolar amounts of a silver(I) scavenger (e.g. AgOTf), complex **3a** delivered the hydroarylation product **4** in 48 % yield. An improved outcome (87 % yield) was observed when thiophene-derived complex **3g** was used, likely as a result of its higher stability (Scheme 7, eq 1).[16] This complex is also an effective catalyst in other reactions, such as the cyclopropanation of styrene with propargylic acetate **5**, which delivered the *cis*-adduct **6** in 84 % yield, together with a minor amount of its *trans*-isomer (Scheme 7, eq 2).[32] Complex **3g** also enabled the intramolecular formal [4+2] cycloaddition between the *N*-allenamide and isoprene, providing the desired adduct **7** with complete chemo- and regio-selectivity (65 % yield,



Scheme 5. Kinetic isotope effects (KIEs) of cyclometalation of **2a**.



Scheme 6. Mechanistic proposal for the C–H auration step.



Scheme 7. Preliminary catalytic applications of model auracycle **3g**. [a] A 48% yield of **4** obtained when using **3a**, instead of **3g**. [b] An additional 11% yield of the *trans*-derivative **6** was also observed.

Scheme 7, eq 3).[33] The reactivity of **3g** in these reactions parallels or even surpasses that of other well-known gold(III) complexes, thus highlighting the synthetic utility of the zwitterionic species presented in this work (See the Supporting Information for details).[16]

Conclusions

In conclusion, we have discovered a new reactivity mode of gold(III) salts with alkenes, based on an intramolecular cascade heteroauration/arylation sequence to give zwitterionic auracyclic species **3** exhibiting a rare C(sp^3)-Au-C(sp^2) bond connection. The cascade process can be controlled with the temperature so that the acyclic alkylgold(III) precursors **2** can be isolated. The remarkable stability of both gold species was exploited to shed light into the nature of the intramolecular C(sp^2)–H auration step. Experimental results based on KIE, Hammett plots and Eyring analysis suggest that the most probable mechanism involves a S_EAr process in which the rate-determining event is the formation of a π-complex that evolves very rapidly to a Wheland intermediate. This further understanding of the C–H auration can impact on the design and development of new gold-catalyzed reactions entailing this type of elemental steps. Finally, the demonstration that these rare gold metalacycles are also catalytically active, can unveil interesting new possibilities in the area of Au(III) catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Cyclometalated · Zwitterionic · KIE · Gold(III) · Cycloauration

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