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Assessing the Role of Counterion in Gold-Catalyzed Dearomatization of Indoles with Allenamides by NMR Studies

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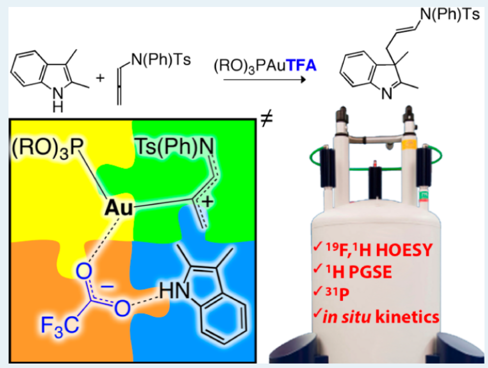
Supporting Information

ABSTRACT: The counterion effect in the gold(I)-catalyzed dearomative condensation of indoles with allenamides is unveiled by means of 1D- and 2D-NMR investigation. The different coordination ability and hydrogen bonding tendency of TFA^- and OTf^- led to specific interactions with the reaction partners dictating the regiodivergent outcome.



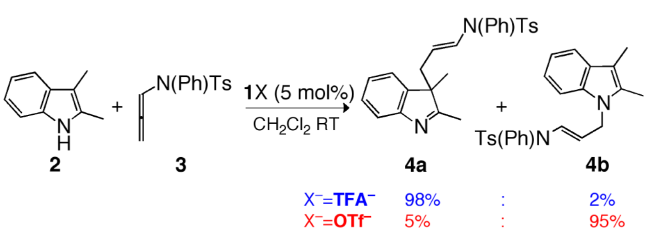
KEYWORDS: *gold, NMR spectroscopy, anion effect, mechanism, weak interactions, homogeneous catalysis*

The counterion is of critical importance in stoichiometric and catalytic reactions of ionic transition metal complexes.[1] Although the number of examples in which the role of counterion is key continuously increases,[2] the rationalization of the counterion action is somewhat hampered usually due to complicated kinetics and to the lack of structural information concerning the localization of the counterion with respect to the ionic metal complex. About 20 years ago,[3] we suggested that NOE NMR interionic studies could be exploited to obtain information on the ion pair structure of ionic transition metal complexes and to correlate the latter with their reactivity.[4] Such a methodology was shown to be particularly successful and was applied, often in combination with diffusion NMR,[5] to provide deeper insights into several important reactions, including olefin polymerization and copolymerization,[6] C–H activation,[7] and small molecule activation by frustrated Lewis pairs.[8]

Among the classes of ionic transition metal complexes successfully used in catalysis, gold(I) linear complexes of general formula [L–Au–S]X (where L = ancillary ligand, S = substrate or solvent, X^- = counterion) are assuming particular importance, especially as far as the activation of unsaturated substrates is concerned.[9] For such complexes, too, X^- plays a critical role,[10] which, in some cases, has been elegantly elucidated by combining NMR, kinetics, and theoretical approaches.[11]

Some of us have very recently documented the role of counterion for the dearomatization of indoles,[12] as a consequence of their reaction with allenamides catalyzed by $[\{2,4\text{-}(^tBu)_2C_6H_3O\}_3P\text{–}Au\text{–}X]$ (**1**X).[13] In particular, it has been shown that the regioselectivity of 2,3-dimethyl-1*H*-indole (**2**) and *N*-tosyl-*N*-phenyl-allen-1-amine (**3**) reaction is dramatically affected by the selection of X^- (Scheme 1).[14]

Scheme 1. Gold-Catalyzed Dearomatization of Indole 2 with Allenamide 3



More precisely, whereas a nucleophilic attack of N(1) at **3** occurs when X^- = OTf^- (OTf^- = triflate, $CF_3SO_3^-$), as expected for 2,3-disubstituted indoles,[15] an unusual C(3) attack at **3** takes place when X^- = TFA^- (TFA^- = trifluoroacetate, CF_3COO^-, Scheme 1).

In order to assess the role of X^- in directing the reaction reported in Scheme 1 and, in particular, rationalize why TFA^- and OTf^- provide almost opposite regioselectivity, anion/

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substrates competitive NMR experiments and in situ kinetics were performed, and the results are reported herein.

1X exhibited a notably different reactivity with **2** when X^- = TFA^- and OTf^-. The NMR spectra of a mixture of **1**TFA and 1.5 equiv of **2**, in anhydrous methylene chloride−d_2, appeared as the sum of the individual spectra of the components in the same solvent, indicating that **1**TFA and **2** were not strongly interacting. This was further confirmed by diffusion NMR experiments, which showed an independent self-translation motion of **1**TFA and **2** in solution. A sensible broadening of both ^{19}F and ^{31}P NMR signals was observed by increasing the amount of indole (Supporting Information). When the temperature was lowered to 233 K, the ^{19}F NMR spectrum resolved in two sharp signals at δ_F = −74.2 and −76.0 ppm having a 60:40 ratio. ^{31}P NMR showed the presence of a principal species at δ_P = 87.8 ppm plus minor species at about 97.0 ppm (ca. 80:20 ratio). ^1H NMR spectrum remained substantially the same. Both the ^{31}P and ^{19}F chemical shift value of the most abundant species is consistent with that of the starting inner sphere **1**TFA. Because the second TFA signal at −76.0 ppm is too intense to account only for outer sphere TFA^- anion belonging to minor gold species, it can be suggested that traces of trifluoroacetic acid, whose signal could be in rapid exchange with that of the anion, formed, likely due to adventitious water.[11c] Consequently, a fraction of minor species could have a counterion different from TFA^-. TFA^- at δ_F = −74.2 ppm showed selective dipolar interactions with both signals due to phosphite ligand and indole in the ^{19}F, ^1H HOESY NMR spectrum recorded at 233 K (Figure 1). In particular, NH and methyl groups in α to the nitrogen atom showed rather strong interactions with the CF_3 moiety of TFA^-, suggesting that hydrogen bonding interactions between an inner sphere anion and the heteroarene were established (Figure 1).

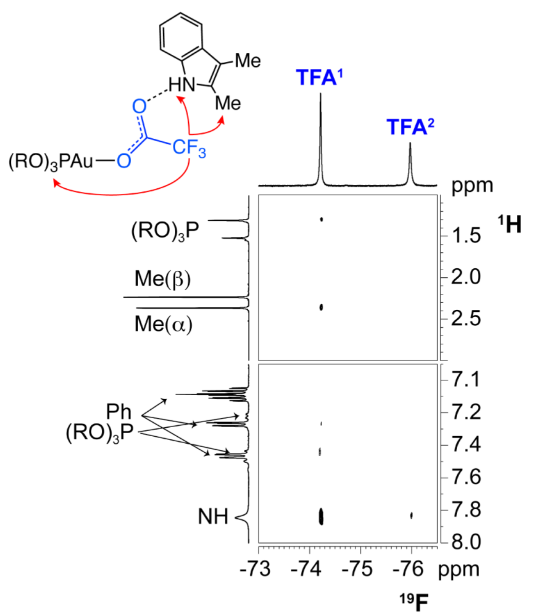
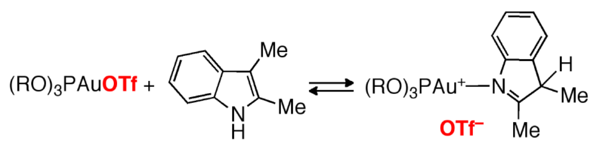


Figure 1. ^{19}F,^1H HOESY NMR spectrum of a mixture containing **1**TFA and 15 equiv of **2** (methylene chloride−d_2, 233 K); red arrows denote NOE interactions.

The second TFA^- signal shows a weak interaction with the NH group in the ^{19}F, ^1H HOESY NMR spectrum (Figure 1), suggesting that also the outer sphere TFA^- anion establishes hydrogen bonding with **2**, even if the presence of transferred NOE cannot be ruled out.[16] The picture emerging is that **2** does not displace easily the TFA^- anion from the first coordination sphere of Au, and only a minor fraction of outer sphere ion pairs is formed. In both types of complexes, the presence of a hydrogen bond donor moiety stimulates the interaction with **2** in a manner which could be important for the catalytic dearomatization reaction.

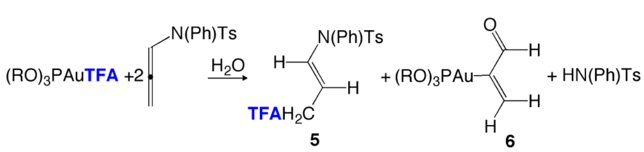
When **1**OTf was reacted with an excess of **2** (ca. 2.5 equiv), a fast reaction took place, and a new signal at δ_P = 97.3 ppm was detected in the $^{31}P\{^1H\}$ NMR spectrum. ^1H NMR spectroscopy revealed the formation of a new set of signals, featuring a quartet at δ_H = 4.0 ($J_{H,H}$ = 7.9 Hz), a singlet at δ_H = 2.46, and a doublet at δ_H = 1.54 ($J_{H,H}$ = 7.9 Hz), while ^{19}F NMR indicated that the resonance due to the anion shifted from δ_F = −77.7 to δ_F = −78.8 ppm. By crossing all the pieces of information coming from 1D and 2D NMR, it is possible to conclude that **2** displaces OTf^- from the first coordination sphere of **1**OTf and coordinates at the gold center through the nitrogen atom. Moreover, a 1,3-proton shift occurs thus leading to the dearomatization of the coordinated indole (indolenine core, Scheme 2). Such a coordination/isomerization of **2** at the gold center showed to be a reversible process, because exchange cross peaks involving free 1H-indole and coordinated 3H-indole were observed in the ^1H NOESY NMR spectrum (Supporting Information). The ^{19}F, ^1H HOESY NMR spectrum of the reaction product (Supporting Information) indicated that the outer sphere OTf^- anion has selective dipolar contacts with the resonances of the phosphite ligand and the methyl group in α position to the nitrogen atom, suggesting that a close Au-anion interaction is present.

Scheme 2. Reactivity of 1OTf with 2



The elucidation of the reactivity of **1**X complexes with allenamide **3** is far more complicated because of collateral reactions arising from the presence of water traces into the reaction environment.[17] Upon mixing **1**TFA with **3** (1.5−15 equiv), in anhydrous methylene chloride−d_2 at 233 K, allene was quantitative converted into an olefinic product formally derived from the addition of a trifluoroacetic acid molecule at **3** (**5**, Scheme 3). At the same time, the majority of the gold complex was converted into a new neutral species **6** featuring an acrolein moiety σ-bonded to the gold center via the C(2) atom (Scheme 3),[18] stemming from the hydrolysis of the allene scaffold.

Scheme 3. Proposed Deactivation Pathway of [Au(I)]-Allene Species in the Presence of Traces of H_2O



Due to this complication coming from adventitious traces of water, a series of in situ NMR reactivity experiments of **1**X with

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3 was carried out with rigorous exclusion of water and oxygen by means of high-vacuum Schlenk techniques (Supporting Information). When **1**TFA was mixed with 1.5 equiv of **3** in dry methylene chloride−d_2 at 233 K, the ^{1}H NMR spectrum of the mixture showed the presence of two sets of signals for both phosphite ligand and allene (Supporting Information). On the other hand, three singlets, located at δ_F = −73.5 (broad), δ_F = −74.3 and δ_F = −75.0 ppm, were observed in the ^{19}F spectrum, and three signals resonating at δ_P = 139.6, δ_P = 130.1, and δ_P = 87.8 ppm were found in the ^{31}P{^{1}H} spectrum, suggesting that three species might be present in solution. The latter ^{31}P signal was straightforwardly assigned to unreacted **1**TFA, which accounts for the 30% of the mixture, indicating that **3** does not displace easily the TFA$^-$ anion from the first coordination sphere of gold. The nature of the other two species **7** and **8** was ascertained by means of ^{1}H, ^{31}P HMBC, ^{19}F, ^{1}H HOESY, and ^{19}F NOESY NMR spectroscopies. In particular, both the signals at δ_P = 139.6 and δ_P = 130.1 ppm showed weak long-range scalar correlations in ^{1}H, ^{31}P HMBC with the broad signal at δ_H = 4.83 ppm (Supporting Information), indicating that both **7** and **8** bear the Au-allene moiety. Importantly, the ^{19}F NOESY spectrum revealed that the resonance at δ_F = −73.6 due to **8** is in selective chemical exchange with the resonance of **1**TFA (Figure 2), strongly suggesting that also **8** is an inner sphere ion pair. Because ^{1}H, ^{31}P HMBC indicates that **3** is also coordinated, **8** has to be formulated as a tricoordinated isip (inner sphere ion pair, Scheme 3).[19]

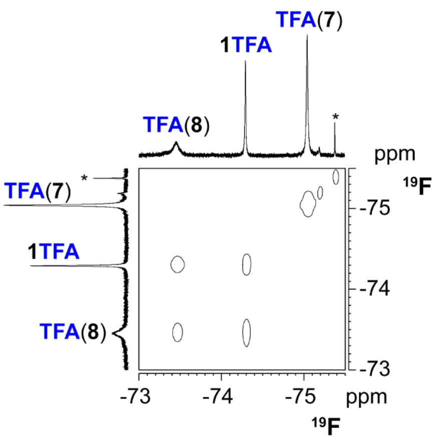
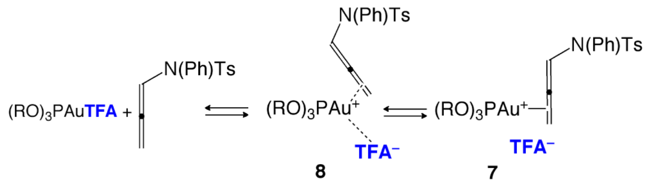


Figure 2. ^{19}F NOESY NMR spectrum of a mixture containing **1**TFA and 1.5 equiv of **3** (dry methylene chloride−d_2, 233 K); asterisk denotes traces of **5**.

Attempts to generate a higher concentration of **8** were carried out by increasing the amount of **3** up to 8 equiv. **1**TFA was consumed quantitatively; nevertheless, the relative concentration of **8** was not sensibly increased compared to that of **7**, suggesting that a steady state concentration of **8** accumulates during **7** formation (Scheme 4).

Consequently, **7** is likely the osip (outer sphere ion pair) derived from the complete displacement of TFA$^-$ by **3**.[20] NMR parameters are consistent with this hypothesis given that the ^{19}F resonance falls at a lower value of chemical shift, because the anion is more negatively charged, and the ^{31}P resonance of **7** falls at a higher chemical shift value than that of **8**, due to the smaller amount of electron density at gold. Another hint to the osip nature of **7** comes from the HOESY spectrum (Supporting Information), which showed that the fluorine signal had rather

Scheme 4. Proposed Reactivity between 1TFA and 3 in Dry Methylene Chloride-d_2 at 233 K



strong dipolar interactions with phosphite ligand signals and two broad signals located at δ_H = 4.83 and δ_H = 6.71 ppm, which were assigned to **3** coordinated at the gold center through the terminal double bond. The signal at δ_F = −73.6 of **8** was too broad to give observable NOEs with protons.

It is interesting to outline that, according to the ^{19}F NOESY experiment, (i) association/dissociation of **3** is faster than association/dissociation of TFA$^-$, and (ii) displacement of TFA$^-$ from gold by **3** occurs through an associative mechanism.

When **1**OTf was combined with 2 equiv of **3** in dry methylene chloride−d_2 at 233 K, ^{1}H NMR spectroscopy indicated that outer sphere ion pairs featuring gold−allene interactions could not be intercepted due to a rapid collateral reaction that consumed all the substrate. Multinuclear and multidimensional NMR studies revealed that **3** quickly dimerized to form disubstituted cyclobutanes (Supporting Information), as previously observed by González.[21] The reaction was found to be catalytic since consecutive addition of **3** just increased the concentration of the product with no apparent modifications of the NMR spectra of **1**OTf.

Finally, to contrast the behavior of **1**TFA and **1**OTf during the catalytic cycle, in situ NMR experiments were performed by using equimolar **2**/**3** mixtures and a catalyst loading of 5−8 mol %. The reactions were sufficiently slow to be monitored by NMR spectroscopy (Figure 3). Both in the cases of **1**TFA and **1**OTf, the first ^{1}H NMR spectrum recorded soon after mixing the reagents showed the presence of unreacted **2** and **3**. ^{31}P{^{1}H} NMR revealed, instead, the formation of a main peak

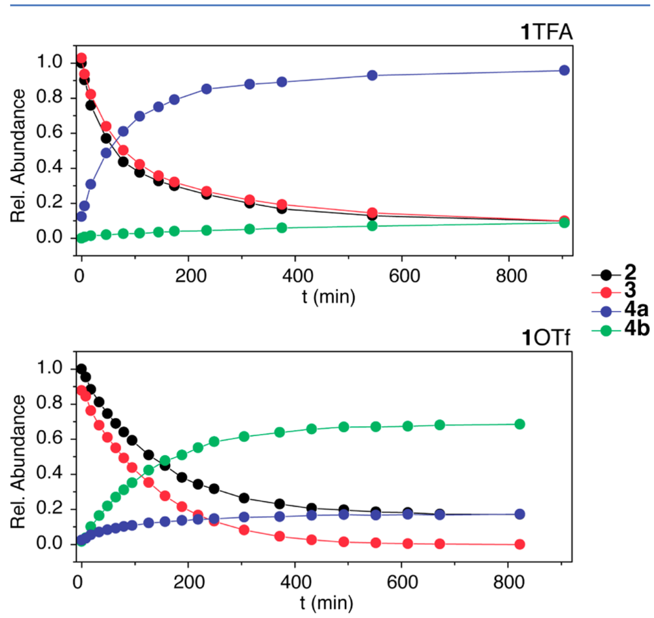


Figure 3. Kinetic profiles for the dearomatization reaction of **2** with **3** catalyzed by **1**TFA and **1**OTf (methylene chloride-d_2, 298 K).

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located at δ_P = 142.0 and δ_P = 140.5 ppm for TFA^- and OTf^-, respectively, which likely indicated the formation of ion pairs featuring **3** in the first coordination sphere of gold.[22] Accordingly, ^{19}F NMR signals of the anions were lower frequency shifted by 1.7 and 1.4 ppm for TFA^- and OTf^-, respectively.

From the kinetic point of view, both the reactions went to completion in about 12 h to give the respective **4a**/**4b** mixture (Supporting Information), indicating that changing the counterion does not alter significantly the overall reaction rate. The concentration versus time trends of **2** and **3** followed a biexponential decay, suggesting that both indole and allene play a role in the rate-determining step. The estimation of the kinetic constants revealed that there is a quite similar kinetics for **4a** and **4b** formation, with a k_{4a}/k_{4b} ratio equal to 13.6 and 0.2 for **1**TFA and **1**OTf, respectively.

Monitoring the reaction mixture by ^{31}P NMR spectroscopy revealed that, in the case of **1**TFA, about one-half of the starting gold−alkene complex was slowly converted into different species during the course of the reaction, having main peaks at $\delta_{P=}$ 97.0, 128.3, and 131.3 ppm. The first one can be assigned as a gold species featuring indole (or product) in the first coordination sphere, whereas the nature of the other two signals is unclear. It can be speculated that they belong to three coordinated species featuring TFA^- in the first coordination sphere of gold, given the similarity with the chemical shift of **8** (Supporting Information). When **1**OTf was used, the starting outer sphere ion pair was instead converted into a new species featuring a phosphite ligand resonating at δ_P = 96.9 ppm, with a kinetics which is exactly the same of that of allene consumption. The similarity between the chemical shift value of the new complex and that of the gold-3H-indole compound led us conclude that the catalyst is converted into a gold complex featuring **4a** in the first coordination sphere. This hypothesis was supported by diffusion NMR, which showed that **4a** and **4b**, having in principle similar hydrodynamic volume values, diffused with different behavior. The observed difference in apparent hydrodynamic dimensions was perfectly in agreement with having the entire gold complex bound to **4a** (Supporting Information for details).

In conclusion, our results show that the difference in coordinating ability and hydrogen bonding tendency of TFA^- and OTf^- plays a remarkable role in driving the reactivity of [{2,4-(^tBu)$_2C_6H_3O$}$_3$P−Au−X] (**1X**) with 2,3-dimethyl-1H-indole (**2**) and *N*-tosyl-*N*-phenyl-allen-1-amine (**3**). In particular, OTf^- anion is not competitive with both substrates for the coordination at the Au(I) center; as consequence, the reaction proceeds by the coordination of **3** at gold followed by the attack of **2** to coordinated **3** via N(1), the most sterically accessible and nucleophilic site, leading to the expected **4b** regioisomer.[14] On the contrary, TFA^- is so coordinating that its displacement from the first coordination sphere of gold occurs only by an excess of **3**. This process possibly leads to the formation of three-coordinated species **8**, successively evolving to osip **7**, in which the anion remains in close proximity to coordinated **3**. Despite **2** is not basic enough to replace the anion, low-temperature NOE studies indicate that it undergoes hydrogen bonding with coordinated TFA^-. All seems to suggest that such N(1)−H···$OCOCF_3^-$ hydrogen bonding interaction, likely occurring in **8**, makes N(1) not available for nucleophilic attack and, at the same time, orients **2** in a way that C(3) might easily attack coordinated **3** leading to **4a**.

Studies addressing the exploitation of these findings in different counterion-controlled gold catalyzed selective organic transformations are currently under investigation in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00502.

General procedures, relevant NMR spectra, and in situ catalytic experiments (PDF)

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Notes

The authors declare no competing financial interest.

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(17) Despite our use of anhydrous methylene chloride, water traces contained in the starting materials were enough to open collateral reaction pathways.

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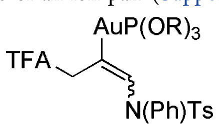
(20) The dynamic nature of these complexes notably hampers the complete NMR characterization. Nonetheless, the possibility that [Au−allene][TFA] complexes exist, in this case, as neutral complexes featuring TFA group in position 1 and Au σ-bonded to C(2) (see below) has been ruled out because the NOE contact of TFA with the CH_2(1) is too weak if compared with that of the phosphite ligand, thus suggesting the presence of an ion pair (Supporting Information).



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(22) ^{31}P chemical shift values are slightly different from those observed in the reaction between **1**TFA and **3**, likely due to the different experimental conditions such as temperature, **1** and **3** concentration, and presence of **2** in the mixture.

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