Introduction

The importance of fluorinated substances is reflected in a wide range of applications in academia and industry. Numerous reports concentrate on selective fluorinations and the introduction of fluorinated substituents, emphasizing the rising interest in fluoroorganic chemistry. The dramatic influence of fluorine or fluorinated substituents on molecular properties renders them indispensable for the modulation of acidity, metabolic stability, lipophilicity, solubility, bioavailability, and binding affinity to target proteins. In homogeneous gold catalysis, various methods are available for the formation of carbon–fluorine bonds. Frequently, these involve the use of electrophilic fluorinating agents like Selectfluor®. There is also a limited number of studies on gold-catalyzed transformations of fluorinated substrates which afford fluorine-tagged heterocycles. Based on our experience in the gold-catalyzed activation of unsaturated molecules (mostly allenes) for regio- and stereoselective cyclization reactions, we now present the first results of a study on the effect of trifluoromethylated substituents on the cyclization of α-hydroxyallenes to 2,5-dihydrofurans.

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Results

Synthetic procedures

For a systematic study of the influence of trifluoromethyl substituents on the reactivity in the gold-catalyzed cycloisomerization, three regioisomeric α-hydroxyallenes 1a–c were synthesized (see ESI for details). For the first part of these investigations, the imidazolium-based ILs and gold catalysts shown in Scheme 1 were used.

The optimization of the reaction conditions was carried out with allene 1a. Different ILs were tested in the presence of 5 mol% AuCl₃ as catalyst (Table 1). Similar to earlier studies, [BMIM][PF₆] gave the shortest reaction time of 4 h (entry 1), while the cyclization in [EMIM][PF₆] is much slower (entry 2). The ionic liquids [EMIM][HSO₄], [BMIM][HSO₄] were used at 60 °C to decrease their viscosity. In this manner, complete consumption of the starting material was detected already after 15 min (entry 3). To rule out the possibility of an acid-catalyzed cyclization in the presence of [EMIM][HSO₄] and [BMIM][HSO₄], the reactions were repeated in the absence of a gold catalyst. No conversion was observed after 24 h (entries 6 & 7). With [EMIM][PO₃][OET₃], [BMIM][BF₄] or [EMIM][BF₄], unsatisfactory results were obtained (entries 8–10). The high reactivity observed in [BMIM][PF₆] may be due to formation of L–Au–OPOF₂ species by fluoride abstraction or hydrolysis of PF₆⁻ by adventitious water.

Next, we investigated the reactivity of allene 1a in [BMIM][PF₆] in the presence of different gold catalysts at room temperature (Table 2). Compared to AuCl₃, the activity of AuBr₃ is much lower (entry 2 vs. 1). In contrast to this, cationic gold(i) complexes afforded full conversion of 1a with only

Gold-catalyzed cycloisomerization of trifluoromethylated allenols: sustainability and mechanistic studies†‡

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Trifluoromethyl-substituted α-allenols are cyclized to the corresponding 2,5-dihydrofurans in the presence of neutral or cationic gold catalysts. The catalyst can be recycled if ionic liquids (in particular [BMIM][PF₆]) are used as reaction medium. The allene forms droplets in the ionic liquid generating a heterogeneous two-phasic system. Kinetic studies in organic solvents using electronically different gold catalysts allowed to identify the protodeauration of a π-gold species as rate-determining step of typical allene cyclizations. Only if a CF₃ group is present at C-5, π-complex formation is rate-limiting.

Dedicated to Prof. Barry M. Trost on the occasion of his 75th birthday.

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reaction takes place. AgSbF₆ itself is a less reactive catalyst, times of 1
plexes conversion (entry 4). In the case of neutral chlorogold(I) com-
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10 [EMIM][BF₄]2 5 2 4 h 0
9 [BMIM][BF₄]2 5 2 4 h 3 0
8 [EMIM][(PO₂)OEt₂]2 5 5 d 9
7 [EMIM][HSO₄]
60 15 min 100
43x308]3 [BMIM][PF₆] 60 15 min 100
3 [BMIM][PF₆] 60 15 min 100
60 24 h 100
6 [BMIM][HSO₄]
3 [BMIM][PF₆] 60 15 min 100
5 mol% catalyst. In the latter case, AuCl₃ and
 Prepared in 1 M pentane in the presence of 5 mol% catalyst.
 prepared in 2 M pentane in the presence of 5 mol% catalyst.
2 mol% catalyst loading. Determined by GC-FID. Allene 1a was
Table 2 Influence of the gold catalyst on the cycloisomerization of α-hydroxyallene 1a to dihydrofuran 2a in [BMIM][PF₆]³⁺
Entry Catalyst mol% Time Conv. b [%]
1 AuCl₃ 5 4 h 100
2 AuBr₃ 5 24 h 100
3 Ph₃PAuNTf₂ 2 1.5 h 100
4 A 2 15 min 100
5 B/AgSbF₆ 2 1 h 100
6 C/AgSbF₆ 2 3 h 100
7 D/AgSbF₆ 2 6 h 100
8 Ph₃PAuCl/AgSbF₆ 2 4 h 100
9 AgSbF₆ 2 3 d 25³
At room temperature. b Determined by GC-FID. c Allene 1a was reisolated.

2 mol% catalyst loading (entries 3–8). The highest activity was
24 h (entries 5–8). Without the silver additive no reaction takes place. AgSbF₆ itself is a less reactive catalyst, leading to 25% conversion after 3 d (entry 9).
After optimization of the reaction conditions, we determined reactivity profiles of the regioisomeric trifluoromethyl-substituted α-hydroxyallenes 1a–c in [BMIM][PF₆] at room temperature (Table 3). Here, catalysts of different reactivity and chemical nature were selected: AuCl₃, Ph₃PAuNTf₂, A, and D/AgSbF₆. Irrespective of the catalyst, the same reactivity order for the three allenols was found: 1a is the most reactive one, followed by 1c, whereas 1b displays the lowest reactivity. In the latter case, AuCl₃ and D/AgSbF₆ afforded incomplete conversion after 24 h at room temperature. Thus, compared to simple non-fluorinated allenes, introduction of a trifluoromethyl substituent causes a strong reactivity decrease.² A consistent reactivity profile for the different gold catalysts was also observed. Catalyst A is the most active one, followed by Ph₃PAuNTf₂ (entries 2 & 3), whereas AuCl₃ (entry 1) and D/AgSbF₆ (entry 4) are less reactive.

Previously, it was demonstrated that gold catalysts in ionic liquids are stable to water, air and organic solvents and thus can be recycled after extraction of the product.³ This technique can also be applied to trifluoromethylated allenes, as shown exemplarily for substrate 1a (Table 4). The dihydrofuran 2a was isolated by extraction with pentane in good yields over five runs, and no loss of the catalytic activity was observed.

Mechanistic studies
To improve the mechanistic understanding of gold-catalyzed transformations in ionic liquids and in organic solvents, several experiments were carried out. First, in order to gather information about the solubility of trifluoromethylated allenes in ionic liquids, we examined an ultrasonicated mixture of

Table 3 Reactivity of α-hydroxyallenes 1a–c towards different gold catalysts in [BMIM][PF₆]³⁺
Entry Allene: [Au] 1a [Time h⁻¹] 1b [Time h⁻¹] 1c [Time h⁻¹]
1 AuCl₃ 5 24³ 24³ 24³
2 A 0.25 1 1 1
3 Ph₃PAuNTf₂ 1.5 6 2.5
4 D/AgSbF₆ 6 24³ 24³
Time required for full conversion (or conversion after 24 h) at room temperature with 2 mol% catalyst, determined by GC-FID. ³ 5 mol% catalyst loading. ³ 45% conversion. ³ 95% conversion. ³ 83% conversion.
Catalyst species in an ionic liquid. Previous studies revealed a significant effect of the IL9,14 and the formation of gold nanoparticles.15 In order to investigate whether the stabilization can be attributed to the formation of gold–NHC complexes, we used [BMMIM][PF6] which, compared to [BMIM][PF6], has an additional methyl substituent in 2-position and cannot form an N-heterocyclic carbene. Moreover, we applied the gold–NHC complexes E and F15 to the cyclization (Table 5).

Both ILs were used at 60 °C to maintain a sufficiently low viscosity (Table 5). It turned out that there is virtually no reactivity difference between [BMIM][PF6] and [BMMIM][PF6] (entries 1 vs. 2; 3 vs. 4; 5 vs. 6). In all cases, a rapid cyclization took place within 5–20 min. Thus, the formation of gold–NHC complexes is not required for the catalytic activity, but it may contribute to the stability of the catalyst in ILs. Remarkably, complex E showed a good catalytic activity after activation with AgSbF6 (entries 7 and 8), while the ionic dimer F is completely unreactive (entry 9). Hence, formation of dimeric gold–NHC complexes of the type F may be a pathway leading to deactivation of the gold catalyst.

The mechanism of the gold-catalyzed endo-selective cycloisomerization of α-functionalized allenes has been studied extensively, leading to the catalytic cycle shown in Scheme 2.7,16 In the first step the π-complex I is generated by coordination of the catalytically active gold species to a C–C-double bond of allene I. The subsequent intramolecular attack of the nucleophile leads to the σ-gold species III. Finally, protodeauration affords the product IV and regenerates the gold catalyst. Due to the observation that the cycloisomerization of simple α-hydroxyallenes is accelerated in the presence of external proton donors, it is assumed that the protodeauration is the rate determining step of this reaction.

In a recent seminal contribution, Wang, Hammond, and Xu have examined the influence of electronically different ligands on the rate of gold-catalyzed transformations. Whereas the activation of an unsaturated substrate (e.g., I → II) can be accelerated by electron-deficient ligands, the rate of the protodeauration of a σ-vinylgold species (e.g., III → IV) can be increased by electron-rich ligands. Thus, the opposing electron demand of the individual reactions can be used to determine the rate-determining step of the catalytic cycle. We first applied Hammond’s method to the gold-catalyzed cycloisomerization of the exemplary non-fluorinated α-functionalized allenes 3a/b which afford the heterocycles 4a/b (Scheme 3).

![Scheme 2](image)

**Scheme 2** Proposed mechanism of the gold-catalyzed cycloisomerization of α-functionalized allenes (X = NR, O, S).

![Scheme 3](image)

**Scheme 3** Gold-catalyzed cycloisomerization of allenes 3a/b.

Table 4  Recycling of the catalyst

| Run | Time [min] | Yield [%] |
|-----|------------|-----------|
| 1   | 15         | 88        |
| 2   | 15         | 90        |
| 3   | 15         | 91        |
| 4   | 15         | 88        |
| 5   | 15         | 81        |

a Reaction conditions: allenol 1a + catalyst A (1 mol%) in [BMMIM][PF6] at room temperature; product extraction with pentane. b Isolated yield.

Table 5  Cycloisomerization of α-hydroxyallene 1a to dihydrofuran 2a with different gold catalysts and ILs

| Entry | [Au]a | IL                  | T [°C] | Time [min] | Conv. [%] |
|-------|-------|---------------------|--------|------------|-----------|
| 1     | AuCl3 | [BMIM][PF6]         | 60     | 15         | 100       |
| 2     | AuCl3 | [BMIM][PF6]         | 60     | 20         | 100       |
| 3     | A     | [BMIM][PF6]         | 60     | 5          | 100       |
| 4     | A     | [BMIM][PF6]         | 60     | 5          | 100       |
| 5     | Ph3PAuNTf2 | [BMIM][PF6] | 60     | 15         | 100       |
| 6     | Ph3PAuNTf2 | [BMIM][PF6] | 60     | 20         | 100       |
| 7     | E/AgSbF6 | [BMIM][PF6] | 25     | 4          | 100       |
| 8     | E     | [BMIM][PF6]         | 25     | 24         | 0         |
| 9     | F     | [BMIM][PF6]         | 25     | 24         | 0         |

a Catalyst loading: 5 mol% (entries 1 & 2); 2 mol% (entries 3–9). b Determined by GC-FID.
Six phosphine- or phosphite-gold complexes were used for this kinetic study; the ligands exhibit decreasing electron-donating ability in the following order: \( B > (4\text{-MeOC}_6\text{H}_4)_3\text{PAuCl} > (4\text{-MeC}_6\text{H}_4)_3\text{PAuCl} > \text{Ph}_3\text{PAuCl} > (4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{PAuCl} > D \). The chlorocomplexes were activated with equimolar amounts of AgOTf. Different solvents and catalyst loadings were tested to find optimal reaction conditions. Reaction times between 1 and 3 h were required in order to gather a sufficient number of samples which were analyzed by gas chromatography. The results obtained for \( \alpha\)-hydroxyallene 3a are shown in Fig. 1. They clearly show that the rate of the cyclization is rising with increasing electron-donating properties of the ligand. In the context of Hammond’s results, this indicates that the protodeauration of the \( \sigma\)-vinylgold species III is the rate-determining step of the catalytic cycle.

The corresponding kinetic study with \( \alpha\)-aminoallene 3b was carried out with four phosphinegold complexes (Fig. 2). Again, electron-rich ligands lead to rapid cyclizations. Thus, also for aminoallene 3b, the protodeauration is the rate-determining step.

Pushing the limits of the accelerating effect of electron-rich phosphine ligands is possible by changing the number and position of electron-releasing groups. This could be demonstrated for the cycloisomerization of allenol 3a with methoxy-substituted phosphinegold complexes (Fig. 3). It turned out that the accelerating effect of the methoxy group in 2-position is stronger than in 4-position. Accordingly, the catalyst formed from \([2,4,6-(\text{MeO})_3\text{C}_6\text{H}_2]_3\text{PAuCl}\) and AgOTf gave by far the fastest cyclization.

Recently, Hammond and co-workers demonstrated that additives with good hydrogen-bond acceptor ability can increase the rate of gold-catalyzed reactions if the protodeauration is the rate-limiting step. We examined this effect for the gold-catalyzed cycloisomerization of 3a with \( \text{Ph}_3\text{PAuCl}/\text{AgOTf} \) in the presence of \([\text{Bu}_4\text{N}]\text{OTf}\) or pyridin-N-oxide (Fig. 4). As expected, both additives accelerate the conversion of allene 3a. This result confirms once more the protodeauration as rate-determining step.

After demonstrating the viability of Hammond’s method for the gold-catalyzed cyclization of allenes 3a/b, we extended our kinetic study to the trifluoromethylated counterparts 1a–c. As already mentioned above, introduction of the electron-with-
drawing CF₃ group causes a strong decrease of reactivity in the gold-catalyzed cyclization. Is this effect accompanied by a change of the rate-determining step? As can be seen in Fig. 5 and 6, this is not the case of allenols 1a and 1b. For both substrates, the electron-rich gold catalysts B and (4-MeOC₆H₄)₃PAuCl gave faster reactions than the electron-poor phosphate–gold complex D. Thus, also for these allenles the protodeauration is rate-limiting.

In contrast to the previous substrates, allenol 1c bearing a trifluoromethyl group at C-5 shows a different kinetic behavior (Fig. 7). Here, the electron-deficient phosphite–gold catalyst D induces the fastest reaction, the electron-rich phosphine–gold complex B the slowest. According to Hammond’s investigations, this indicates that the activation of the allene with formation of π-complex II is the rate-determining step of the catalytic cycle.

With our kinetic study, we could show for the first time that the rate-determining step of a gold-catalyzed transformation can be changed by variation of the electronic properties of the substrate. It appears that in the case of allenol 1c, the electron-withdrawing effect of the CF₃ group at C-5 causes a strong decrease of electron density at the adjacent C-C double bond.

As a consequence, formation of π-complex II is slowed down to such an extent that this step becomes rate-limiting. Unfortunately, due to the heterogeneous nature of the reaction mixture in ILs (see above), it is not possible to conduct these kinetic studies in ionic liquids. In the future, we will include steric effects, as well as the influence of the counterion of cationic gold catalysts, in these mechanistic studies.

Conclusions

In this study, we have demonstrated that trifluoromethyl-substituted α-allenols can be cyclized to the corresponding 2,5-dihydrofurans in the presence of neutral or cationic gold catalysts. When ionic liquids (in particular [BMIM][PF₆]) are used as reaction medium, the sustainability of these transformations is improved since a recycling of the gold catalyst becomes possible. Distinct reactivity differences between the allenens 1a–c and the gold catalysts were noted. The allenles form droplets in ionic liquids generating a heterogeneous two-phase system. As a result, diffusion and interface exchange processes may have a strong influence on the rate of the reaction. The formation of gold–NHC complexes is not required for the catalytic activity, but it may contribute to the stability of the catalyst in ILs. Extensive kinetic studies in organic solvents using phosphine- or phosphite–gold catalysts with different electronic properties allowed to identify the protodeauration of α-gold-species III as rate-determining step of the catalytic cycle for fluorinated allenens 1a/b, as well as for the non-fluorinated substrates 3a/b. In contrast, activation of the allene with formation of π-complex II is the rate-limiting step for substrate 1c. This mechanistic change (which has been determined for the first time for a gold-catalyzed transformation) is probably caused by the electron-withdrawing effect of the CF₃ group at C-5 which strongly decreases the electron density of the adjacent C-C double bond. Our study underlines the importance of sustainable reaction conditions, as well as, mechanistic investigations for the improvement of catalytic processes. Further work along these lines is in progress.
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