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A Cationic Gold(I) Complex as a General Catalyst for the Intermolecular Hydroamination of Alkynes: Application to the One-Pot Synthesis of Allenes from Two Alkynes and a Sacrificial Amine

Xiaoming Zeng, Guido D. Frey, Shazia Kousar, and Guy Bertrand*^[a]

Carbon-carbon and carbon-nitrogen bond formations are at the heart of modern organic chemistry. The development of novel coupling strategies that facilitate the rapid and efficient construction of complex molecules remains a preeminent goal in synthetic chemistry. For a long time, allenes have been considered as chemical curiosities.^[1] Nowadays, these cumulenes are not only used as building blocks for the synthesis of complex molecules,^[2] but because of the intriguing biological properties of many allenic natural products, the C=C=C skeleton is often introduced in pharmacologically active classes of compounds.^[3] Consequently, despite a number of synthetic routes known, new efficient preparative methods are highly desirable. Of special interest are catalytic processes, which directly build the three-carbon allene core by coupling two different fragments, thus allowing for convergent synthesis. The first of such processes was discovered in 1979, namely the Crabbé homologation^[4] (Scheme 1a). This is a CuBr mediated three-component reaction between a terminal alkyne, formaldehyde, and diisopropylamine. The most important drawback of this process is that ketones and even aldehydes cannot be used in place of formaldehyde, and thus only mono-substituted allenes can be produced. In 2000, Barrett reported a few examples of allene cross metathesis,^[5] which allow one of the terminal carbon units of a preformed allene to be exchanged to yield a new symmetrically substituted 1,2-diene, although extensive polymerization side reactions occur (Scheme 1b). More recently, we have shown that cationic Au^{I} complex A_{1} efficiently mediates the catalytic coupling of enamines and terminal alkynes to yield allenes^[6] (and not propargyl amines

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Scheme 1. a) Crabbé homologation; b) Allene metathesis; c) Gold(I) catalyzed cross-coupling of enamines and terminal alkynes; d) Synthetic strategy; e) Synthesis of cationic gold(I) complexes A_1 .

as observed with other catalysts),^[7] along with the corresponding imines (Scheme 1 c). For this process all types of terminal alkynes can be used, as well as mono-, di-, and trisubstituted enamines; however the latter have to be tertiary derivatives, and one of the *N*-substituents an alkyl group with a hydrogen atom next to nitrogen, in order to deliver a hydrogen. The tertiary enamines are formally hydroamination adducts of alkynes with secondary amines.^[8] Therefore, we reasoned that if the gold complex **A**₁ were also able to catalyze the addition of secondary amines to alkynes,^[9] it would be possible in one-pot reactions to form allenes from two alkynes and a secondary amine; formally, the only restriction would be the use of a terminal alkyne for the second step (Scheme 1 d).

Despite tremendous progress in identifying efficient catalysts for the intermolecular addition of amine derivatives to alkynes, real difficulties remain with secondary amines,^[8–12] partly because early transition metals cannot be used, due

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 [[]a] X. Zeng, Dr. G. D. Frey, S. Kousar, Prof. G. Bertrand UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957) Department of Chemistry University of California Riverside, CA 92521-0403 (USA) Fax: (+1)951-827-2725 E-mail: guy.bertrand@ucr.edu

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to the involvement of an imido complex (L_xM=NR) in the catalytic cycle.^[13] Uchimaru^[14] reported that a ruthenium cluster was efficient but the scope of the reaction was strictly limited to arylacetylenes and N-methyl aniline; moreover a 10-fold excess of amine was necessary. Schmidt^[15] described the addition of morpholine (62% yield) and piperidine (38% yield) to phenylacetylene in the presence of palladium(II) 3-iminophosphine complexes; in this case, a 10fold excess of alkyne was necessary due to the competing cyclotrimerization of phenylacetylene. Lastly, there is only one report concerning the hydroamination of internal alkynes with secondary amines. In 2005, using 10 mol% of the aquapalladium complex [Pd(dppe)(H₂O)₂](TfO)₂, Yamamoto^[16] reported the addition of N-methylaniline to diphenylacetylene and phenyl(butyl)acetylene in good yields. Clearly general catalytic systems able to promote the intermolecular hydroamination of alkynes, especially with basic secondary amines are still missing.

Recently, we have shown that the cationic gold(I) complex A_1 (Scheme 1),^[17,18] featuring a bulky cyclic (alkyl)-(amino)carbene (CAAC),^[19] as ancillary ligand, efficiently promotes the addition of ammonia to non-activated alkynes.^[20] These first examples of homogeneous catalytic hydroamination with ammonia hinted at the possibility of a general catalyst for the hydroamination of alkynes with secondary amines.

Here we report that complex A_1 catalyzes the addition of many types of non-tertiary amines to terminal as well as internal alkynes, and the first examples of intermolecular hydroamination of internal alkynes with secondary alkyl amines. Moreover, we show that addition of a terminal alkyne to the in situ formed enamines, allows for the synthesis of a variety of allenes without any additional catalyst.

Since several catalytic systems are known to promote the hydroamination of alkynes with primary amines, we briefly investigated if complex A_1 , prepared by mixing the corresponding [(CAAC)AuCl] A complex with one equivalent of $KB(C_6F_5)_4$ (Scheme 1e) was efficient as well. We chose the bulky mesitylamine 1, as an example of arylamine, and six different alkynes **a**-**f**, which are representative of all types of simple acetylene derivatives (Table 1). In all cases (entries 1-6), clean reactions occurred (81-94% yield) at temperatures between 40 and 140°C, and a reaction time between 10 to 24 h, using 5 mol% of A₁. Not surprisingly, a mixture of Markovnikov and anti-Markovnikov products were obtained when methylphenylacetylene c and tert-butylacetylene e were used (entries 3 and 5), although with cyclohexylacetylene f, only the Markovnikov product was obtained (entry 6). Since the reaction with 3-hexyne required the most drastic conditions, this substrate was used to test a primary alkylamine, and we chose the bulky tert-butylamine (entry 7). We were pleased to observe that after 12 h at 140 °C, the hydroamination adduct was obtained in 81 % yield (as a 55/45 mixture of E and Z isomers), indicating the broad applicability of our catalytic system.

These quite promising results prompted us to investigate the hydroamination of alkynes with secondary amines. Table 1. Hydroamination of alkynes **a-f** with primary amines **1** and **2**.^[a]



[a] A_1 (5 mol%), amine (0.5 mmol), alkyne (0.5 mmol), C_6D_6 (0.4 mL). [b] Yields are determined by ¹H NMR using benzylmethyl ether as an internal standard.

Table 2 shows that diarylamine 3, arylalkylamine 4, benzocyclic amine 5, and even dialkylamine 6 add to terminal alkynes **a**, as well as internal alkynes **b**-**d** at temperatures between 60 to 120°C, and reaction times between 7 to 24 h, using 5 mol% of A_1 . The only noticeable difficulties have been found with phenylacetylene a (except entry 1), because of competitive oligomerization processes. With phenylacetylene **a** (entries 1, 3, 7, 11) and diphenylacetylene **b** (entries 4, 8, 12) the Markovnikov adduct and the E isomer, respectively, were exclusively formed. With methylphenylacetylene \mathbf{c} , in most cases, the expected mixture of Markovnikov and anti-Markovnikov products were obtained (entries 2, 5, 9, 13) but more surprising are the results observed with diethylacetylene **d** (entries 6, 10, 14). Indeed, we observed that the expected hydroamination adduct was only the minor product (21-43%) of the reaction, the major product (79-57%)being an isomer in which the unsaturation has been shifted. So far, we have no explanation for this isomerization. However, as can be seen below, this is not a hurdle for the next step of the cascade reaction leading to allenes.

Then, having demonstrated that complex A_1 allowed for the synthesis of tertiary enamines, with alkyl substituents at nitrogen, we investigated the one-pot preparation of allenes by coupling two alkynes, using a sacrificial secondary amine (Scheme 1 d). Our synthetic strategy was first checked by studying the homocoupling of *tert*-butylacetylene **e**. A deuterated benzene solution of alkyne with 0.5 equivalent of various amines was heated at 120 °C for 16 h, in the presence of 5 mol% of A_1 . As shown in Scheme 2, (methyl)-

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| Entry | Amine | Alkyne | $T [^{\circ}C]$ | <i>t</i> [h] | Product | Yield ^[b] |
|-------|-------|--------|-----------------|--------------|---|----------------------|
| 1 | 3 | a | 80 | 7 | Ph ₂ N Ph | 95 |
| 2 | 3 | c | 120 | 16 | $\frac{Ph_2N}{E Z: 1.2}$ | 48 |
| 3 | 4 | a | 70 | 8 | PhMeN Ph | 70 |
| 4 | 4 | b | 120 | 16 | PhMeN Ph Ph | 98 |
| 5 | 4 | c | 120 | 16 | PhMeN | 98 |
| 6 | 4 | d | 120 | 16 | PhMeN PhMeN Et 21% Et nPr 79% | 86 |
| 7 | 5 | a | 60 | 12 | | 46 |
| 8 | 5 | b | 90 | 24 | | 96 |
| 9 | 5 | c | 120 | 16 | CN 48% Ph Ph 52% | 67 |
| 10 | 5 | d | 110 | 20 | CN Et 42% Et nPr 58% | 85 |
| 11 | 6 | a | 100 | 12 | Et ₂ N Ph | 23 |
| 12 | 6 | b | 90 | 20 | Et ₂ N Ph Ph | 98 |
| 13 | 6 | c | 120 | 20 | Et ₂ N Et ₂ N Ph Ph Ph 43% | 89 |
| 14 | 6 | d | 110 | 16 | | 94 |

| Table 2. | Hydroamination | of alkynes a- | with secor | ndary amines 3–6 . ^[a] |
|----------|----------------|---------------|------------|--|
|----------|----------------|---------------|------------|--|

[a] A_1 (5 mol%), amine (0.5 mmol), alkyne (0.5 mmol), C_6D_6 (0.4 mL). [b] Yields are determined by ¹H NMR using benzylmethyl ether as an internal standard.

(benzyl)amine, dibenzylamine 7 and 1,2,3,4-tetrahydroisoquinoline 5 were the most efficient amines, the expected allene 8a being formed in 59, 61 and even 89% yield, respectively.

Allene **8a** results from the anti-Markovnikov addition of the amine to the *tert*-butylacetylene \mathbf{e} ; a similar regioselectivity was observed with trimethylsilylacetylene, as expected because of the steric hindrance of both reactants. With *n*butylacetylene, the allene **9**, resulting from the Markovnikov addition of the amine, was formed in 68% yield, whereas with cyclohexylacetylene a 14/86 mixture of the two isomeric allenes **8** and **9** was obtained in 79% yield (Scheme 3).

To expand the scope of our catalytic process, we investigated the cross-coupling reaction of alkynes (Table 3). Benzene solutions of an internal alkyne and 0.9 equivalent of 1,2,3,4-tetrahydroisoquinoline **5** or dibenzylamine **7** were first heated at 120 °C, in the presence of 5 mol % of A_1 . The reactions were monitored by NMR spectroscopy, and after complete conversion of the amine, 0.9 equivalent of a terminal alkyne was added to the reaction mixtures. After heating for 16 h at 130 °C, we were pleased to find that the expected allenes were formed in good to excellent yields. Indeed, the cross-coupling of 3-hexyne and a set of four different terminal alkynes afforded the corresponding allenes **10** in 73 to



Scheme 2. Influence of the amine on the homo-coupling of *tert*-butyl-acetylene.



Scheme 3. Gold-catalyzed homo-coupling of various alkynes in the presence of 1,2,3,4-tetrahydroisoquinoline **5**.

Table 3. Gold-catalyzed hetero-coupling of various alkynes in the pres-enceof1,2,3,4-tetrahydroisoquinoline5ordibenzylamine7.

| R ¹ | $= R^2 \frac{1}{2}$ | 5 or 7 (1 | 0.9 Eq.), ═───H, (0 | A₁ (5 mol%).9 Eq.), 13 | + -); 120 °C F 0 °C F | $\stackrel{1}{\longrightarrow} \stackrel{1}{\longrightarrow} \stackrel{1}$ | R^2 R^1 R^2 |
|----------------|---------------------|----------------|------------------------|------------------------------------|-----------------------------------|--|-------------------------|
| Entry | Amine | \mathbf{R}^1 | \mathbf{R}^2 | \mathbb{R}^4 | 10 [%] | 11 [%] | Yield ^[b] |
| 1 | 7 | Et | Et | tBu | 100 | 0 | 83 |
| 2 | 5 | Et | Et | <i>n</i> Bu | 100 | 0 | 95 |
| 3 | 5 | Et | Et | cHex | 100 | 0 | 82 |
| 4 | 5 | Et | Et | Ph | 100 | 0 | 73 |
| 5 | 7 | Ph | Me | tBu | 57 | 43 | 61 |
| 6 | 7 | Ph | Me | <i>n</i> Bu | 65 | 35 | 64 |
| 7 | 7 | Ph | Me | cHex | 60 | 40 | 59 |

[a] Yields are determined, based on the amine, by ¹H NMR using benzylmethyl ether as an internal standard.

95% yield (Table 3, entries 1–4). Note that although two isomeric hydroamination products are formed (see, Table 2, entries 6, 10 and 14), both of them lead, as expected,^[21] to only one allene. When the unsymmetrical methylphenylacetylene was used, two isomeric allenes **10** and **11**, arising from the Markovnikov and anti-Markovnikov hydroamination products, were obtained in reasonable yields (Table 3, entries 5–7).

These results, in addition to those previously reported on the hydroamination with ammonia,^[20] demonstrate that $[(CAAC)Au]^+ [B(C_6F_5)]^-$ complex A_1 is a very general precatalyst for the addition of amines to alkynes. It is of note that Tanaka^[22] reported that a cationic gold(I) complex, similar to A_1 , but bearing triphenylphosphine as an ancillary ligand (prepared from $[(Ph_3P)AuCH_3]$ and an acidic promoter), promoted the intermolecular hydroamination of terminal as well as internal alkynes with a variety of primary arylamines, but the protocol did not tolerate alkylamines and secondary amines.^[23] The comparison of Tanaka's results with our findings, clearly demonstrates the specific properties of the CAAC ancillary ligand.

The coupling of two alkynes to form allenes, using an amine as a two hydrogen donor, is one of the very few known processes^[24] that combines two very distinct chemical reactions, yet relies on a single catalyst. Since gold complexes^[25] feature little oxophilic character, and thus display excellent functional group tolerance and low air and moisture sensitivity, this one-pot catalytic protocol should find applications in the synthesis of complex molecules.

Experimental Section

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Water- and oxygen-free solvents were employed.

General procedure for the hydroamination reactions: In a dried J-Young-Tube, [(CAAC)AuCl] complex **A** (15 mg, 0.025 mmol) and KB(C_6F_5)₄ (16 mg, 0.025 mmol) were loaded under an argon atmosphere. C_6D_6 (0.4 mL) and the internal standard, benzyl methyl ether, were added and after shaking the tube, the alkyne (0.5 mmol) and amine (0.5 mmol) were loaded. The tube was sealed, placed in an oil bath behind a blast shield, and heated at the specified temperature. The reaction was monitored by NMR spectroscopy. The products were purified by removal of the solvent and extraction with *n*-hexane.

General procedure for the catalytic homocoupling of alkynes: Same experimental conditions as above, but 1.0 mmol of terminal alkyne, and heating at 120 °C for 16 h. The products were purified by column chromatography.

General procedure for the catalytic cross-coupling of alkynes: In a dried J-Young-Tube, [(CAAC)AuCl] complex **A** (15 mg, 0.025 mmol) and KB- $(C_6F_5)_4$ (16 mg, 0.025 mmol) were loaded under an argon atmosphere. C_6D_6 (0.4 mL) and the internal standard benzyl methyl ether were added and after shaking the tube, internal alkyne (0.55 mmol) and amine (0.5 mmol) were loaded. The tube was sealed, placed in an oil bath behind a blast shield, and heated at 120 °C, and the reaction was monitored by NMR spectroscopy. After complete conversion of the reactants, a terminal alkyne (0.5 mmol) was added, and the reaction mixture heated at 130 °C for 16 h. The products were purified by column chromatography.

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