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Gold Catalysis

Silver-Free Two-Component Approach in Gold Catalysis: Activation of [LAuCl] Complexes with Derivatives of Copper, Zinc, Indium, Bismuth, and other Lewis Acids

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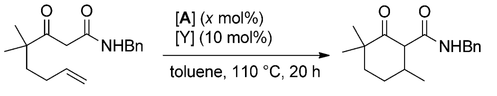
Abstract: Complexes of type [LAuCl] (L = phosphine, phosphite, NHC and others) are widely employed in homogeneous catalysis, however, they are usually inactive as such and must be used jointly with a halide scavenger. To date, this role has mostly been entrusted to silver salts ($AgSbF_6$, $AgPF_6$, $AgBF_4$, AgOTf, etc.). However, silver salts can be the source of deactivation processes or side reactions, so it is sometimes advisable to use silver-free cationic gold complexes, which can be difficult to synthesize and to handle compared with the more robust chloride. We show in this study that various Lewis acids of the transition and main group metal families are expedient substitutes to silver salts. We have tested Cu^I, Cu^{II}, Zn^{II}, In^{III}, Si^{IV}, Bi^{III}, and other salts in a variety of typical Au^I-catalyzed transformations, and the results have revealed that [LAuCl] can form active species in their presence.

Introduction

The cationic gold(I) complexes $[LAu]^+$ are soft Lewis acids that are able to trigger numerous types of nucleophilic attacks onto alkenes, allenes, and alkynes. Over the past 12 years, a myriad of exquisite transformations have been reported in this field.[1,2] In many cases, the cationic gold complexes are generated directly in the reaction vessel and not isolated. A convenient way to do so from stable precursors is to use a gold(I) halide and a silver salt as halide scavenger. The possible interference of silver in the catalytic process notwithstanding,[3] this method avoids the use of strong Brønsted acids and is probably the most popular.[4,5] The reason for this popularity is that the anion metathesis process is rapid and irreversible with silver. We recently pointed out that the efficiency of the halide abstraction could actually be detrimental to the overall efficiency of the catalytic process.[6] The cationic gold complex is sometimes sensitive to some organic materials and decomposes into nanoparticles (or molecular gold clusters) and inactive complexes.[7,8] This phenomenon is accelerated when the concentration of the substrate is increased, or at elevated temperature. We showed that a gradual delivery of the cationic gold(I) complex from its stable halide precursor could maintain the concentration low enough to circumvent the fast destruction of the active species, even at high temperature. To achieve this goal, copper(I) or copper(II) salts were used instead of silver. In our preliminary communication,[6] the usefulness of copper additives was shown on a short set of five reactions, including the intramolecular hydroalkylation of **1a** into **2a** (Table 1) by using either $[(Ph_3P)AuCl]$ or [(JohnPhos)AuCl] (**A**; Figure 1). In spite of the high temperature required for this transformation, full conversion could be reached with the Au/Cu system with loadings of gold as low as 0.1 mol%.

We report herein the fruits of a larger study on the Au/Cu catalytic system and perspectives on the possible additives that can be used instead of silver salts in Au^I-catalyzed transformations.

Table 1. Previous work on Au^I/Ag^I versus Au^I/Cu^I and Au^I/Cu^{II} catalytic systems in the intramolecular hydroalkylation of ene-β-ketoamide **1a**.



1a **2a**

Entry	[Y]	x [mol%]	Conv. [%][a]	d.r.[a]
1	AgOTf	–	0	–
2	AgOTf	0.1	28	n.d.
3	$[(MeCN)_4CuPF_6]$	–	0	–
4	$[(MeCN)_4CuPF_6]$	10	100	87:13
5	$Cu(OTf)_2$	–	15	–
6	$Cu(OTf)_2$	0.1	100	95:5

[a] Estimated by ^1H NMR spectroscopic analysis; diastereomeric ratios shown are *trans/cis*; 100% conversion corresponds to 80% isolated yield.

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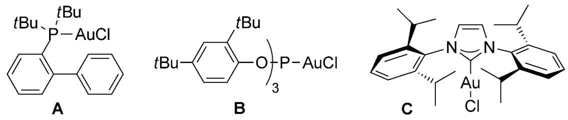
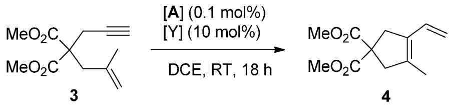


Figure 1. Gold complexes used in this study.

Table 2. Au^I/Ag^I versus Au^I/Cu^I and Au^I/Cu^{II} catalytic systems in the skeletal rearrangement of enyne **3**.



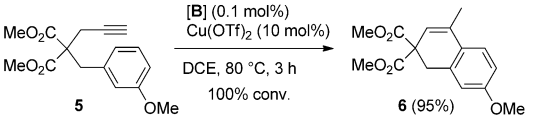
Entry	[Y]	Conv. [%][a]
1	AgOTf	100[b]
2	$Cu(OTf)_2$	100[b–d]
3	$[(MeCN)_4CuPF_6]$	100[e]
4	$[(MeCN)_4CuBF_4]$	79[f]

[a] Estimated by ^1H NMR spectroscopic analysis; 100% conversion corresponds to 80% isolated yield. [b] 100% conversion reached in 3 h. [c] No conversion without gold; no conversion with TfOH instead of $Cu(OTf)_2$. [d] Still 100% conversion with 5 mol% $Cu(OTf)_2$. [e] 10% conversion without gold. [f] 17% conversion without gold.

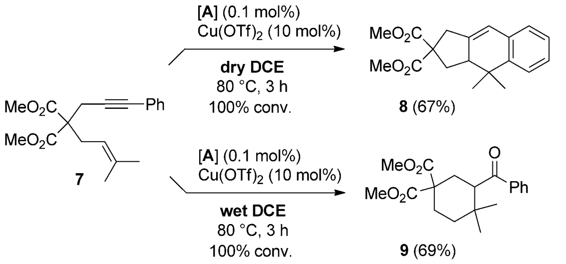
Results and Discussion

Among typical gold-catalyzed transformations, we investigated Au^I/Cu^I and Au^I/Cu^{II} catalytic mixtures in the cycloisomerization of enyne **3** into 1,3-diene **4** (Table 2). In each test, a low loading of 0.1 mol% of [(JohnPhos)AuCl] (**A**) was used together with 10 mol% of activator. Under such conditions, AgOTf provided the expected product[9] with full conversion (entry 1). Interestingly, $Cu(OTf)_2$ and $[(MeCN)_4CuPF_6]$ proved to be equally efficient (entries 2 and 3). On the other hand, the use of $[(MeCN)_4CuBF_4]$ resulted in a lower conversion (79%; entry 4). Because copper complexes are sometimes potent cycloisomerization catalysts,[10] they were also used in the absence of gold, however, no conversion was observed with $Cu(OTf)_2$ alone, and only 10 and 17% conversion were obtained with the Cu^I complexes. Thus, copper salts represent expedient alternatives to more sensitive silver salts, even with simple alkenes as nucleophiles.[11]

Hydroarylation of arenyne **5** was also attempted with the Au/Cu catalytic system (Scheme 1) in a reaction that was previously described with $GaCl_3$ as catalyst.[12] Gratifyingly, product **6** could be isolated in 95% yield when using 0.1 mol% gold and 10 mol% copper. For this reaction, the phosphite gold complex **B**[13] was found to be slightly more efficient than **A**.



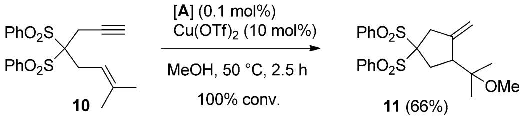
Scheme 1. Use of a phosphite–gold complex in the intramolecular Au/Cu-catalyzed hydroarylation of arenyne **5**.



Scheme 2. Au/Cu-catalyzed [4+2] versus hydrative cyclization of enyne **7**.

Reactions combining carbocyclizations and incorporation of oxygenated nucleophiles were then investigated. In the absence of water, arylenyne **7** transformed into the expected formal [4+2] cycloadduct **8**[14] by using **A** and $Cu(OTf)_2$ in anhydrous 1,2-dichloroethane (Scheme 2). Of particular interest, a hydrative cyclization took place in wet 1,2-dichloroethane, providing ketone **9**. Whereas a few Au-catalyzed hydrative cyclizations have been described,[15] such a reaction has, to the best of our knowledge, been reported only once with $PtCl_4$ as catalyst.[16] Beyond its synthetic interest, this reaction demonstrates the compatibility of the Au/Cu catalytic system with water.

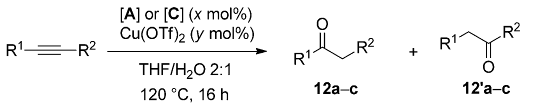
Apart from toluene and dichloroethane, methanol could also be used as solvent. In a typical transformation of enyne **10** into **11**, methanol also serves as nucleophile.[9] Again, the Au/Cu catalytic system proved potent in this alkoxycyclization reaction in which the amount of gold was maintained at 0.1 mol% (Scheme 3).



Scheme 3. Au/Cu-catalyzed alkoxycyclization of enyne **10**.

Because water seems well-tolerated by the Au/Cu catalytic system, we next turned our attention to triple bond hydration.[17] Although the amount of silver was not controlled, it was shown that a mixture of [(IPr)AuCl] (down to 10 ppm) and $[AgSbF_6]$ (tip of spatula) could efficiently promote the addition of water onto alkynes at 120 °C for 18 h in a mixture of 1,4-dioxane/H_2O (2:1).[18] In our tests, a controlled amount of $Cu(OTf)_2$ was used with either [(JohnPhos)AuCl] (**A**) or [(IPr)AuCl] (**C**) in a THF/H_2O mixture (2:1; Table 3).[19] The copper salt alone proved to be unable to catalyze the hydration of 3-hexyne (entry 1), however, with 0.1 mol% **A** and 1 mol% $Cu(OTf)_2$, full conversion could be reached. Reducing the loading of gold to 0.001 mol% resulted in a dramatic decrease in activity (entry 3). As with the Au/Ag system,[18] the use of the NHC gold complex **C** instead of a phosphine gold complex resulted in a more active catalytic mixture, and 60% conversion was achieved with 0.001 mol% gold (entry 4). With diphenylacetylene (entries 5–8), an alkyne for which hydration

Table 3. Au^I/Cu^{II}-catalyzed alkyne hydration.

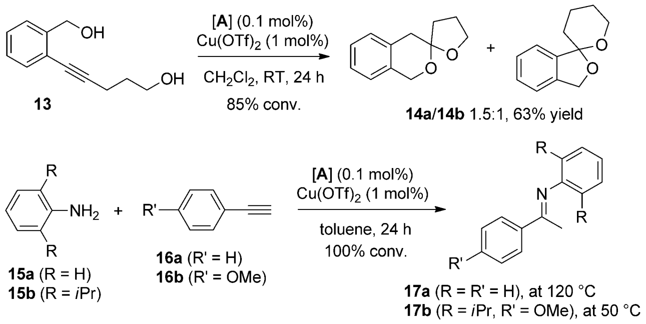


Entry	R^1	R^2	[Au]	x [mol %]	y [mol %]	Product	Conv. [%][a]
1	Et	Et	none	–	1	**12a**	0
2	Et	Et	**A**	0.1	1	**12a**	100[b]
3	Et	Et	**A**	0.001	1	**12a**	27[c]
4	Et	Et	**C**	0.001	1	**12a**	60
5	Ph	Ph	**A**	0.1	1	**12b**	9
6	Ph	Ph	**C**	0.1	1	**12b**	29
7	Ph	Ph	**A**	1	10	**12b**	48
8	Ph	Ph	**C**	1	10	**12b**	100
9	Ph	Bu	**C**	1	10	**12c**+**12′c**[d]	100

[a] Estimated by ^{1}H NMR spectroscopic analysis. [b] 97 % conversion (87 % isolated yield) in dioxane/H_2O (2:1). [c] After three days (16 % conv. after 16 h). [d] Ratio **12c**/**12′c** 1:2.3.

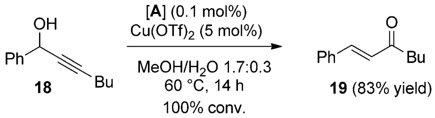
proved more difficult than others with the Au/Ag system,[18] complex **C** again proved to be more efficient than **A**. To gain full conversion, 1 mol % **C** and 10 mol % $Cu(OTf)_2$ were used (entry 8). This combination was also applied to the hydration of hex-1-ynylbenzene, which, similar to the results described for unsymmetrical internal alkynes, gave a regioisomeric mixture of ketones, albeit with full conversion (entry 9). Thus, the Au/Cu mixture is also active in alkyne hydration. It is also worth noting that phosphine, phosphite, and carbene gold chlorides (**A**, **B**, and **C**) were compatible with the Au/Cu system.

The versatility of the Au/Cu approach was further demonstrated with hydroalkoxylation and hydroamination of alkynes (Scheme 4). The formation of regioisomeric spiro compounds **14a** and **14b** has been described by using a trace amount of a NAC-Au^I precatalyst and $AgSbF_6$.[20] On the other hand, hydroamination with low loadings of gold have been performed by using a silver-free cationic gold catalyst displaying a perhalogenated carba-*closo*-dodecaborate anion.[21] Using 1 mol % $Cu(OTf)_2$ and no gold, only 6 % conversion of **13** could be reached under the stated conditions. With 0.1 mol % **A** and 1 mol % $Cu(OTf)_2$, 85 % of **13** converted cleanly into **14a** and **14b**. As for the hydroamination reactions, no reaction took place with **15a**/**16a** and **15b**/**16b** with copper only. With the Au/Cu mixture, **15a**/**16a** and **15b**/**16b** were fully transformed into the corresponding imines **17a** and **17b**. Although the loadings of gold are higher than those reported for these two reactions, it is nonetheless interesting to note that a relatively unsophisticated and commercially available gold complex can be used in combination with a simple copper salt, with both being employed in reasonable amounts.



Scheme 4. Au/Cu-catalyzed hydroalkoxylation and hydroamination of alkynes.

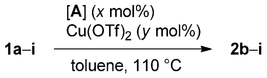
Transformations of propargyl esters and propargyl alcohols represent an important facet of gold catalysis.[22] In particular, α,β-unsaturated ketones can be synthesized directly from propargyl alcohols under Au^I and Au^{III} catalysis (Meyer–Schuster rearrangement).[23] For instance, the transformation of **18** into **19** (Scheme 5) has been described using [(IPr)AuCl]/$AgSbF_6$ (2 mol % each) in a mixture of methanol and water. With the Au/Cu system (0.1 mol % **A** and 5 mol % $Cu(OTf)_2$), full conversion of **18** was also observed.



Scheme 5. Au/Cu-catalyzed Meyer–Schuster rearrangement of compound **18**.

Although for the reactions described above, copper appears to be simply a cost-effective and light-resistant alternative to silver, reactions in which a net increase of efficiency takes place have been clearly identified,[6] among which is the hydroalkylation of unactivated alkenes.[24] To complete our initial study, which was limited to the ene-β-ketoamide **1a** (see Table 1), we carried out the cyclization of substrates **1b–i** displayed in Figure 2 using **A** and $Cu(OTf)_2$ to give products **2b–i**. The results are summarized in Table 4.

Table 4. Au^I/Cu^{II}-catalyzed intramolecular hydroalkylation of β-ketoesters and β-ketoamides.



Entry	Substrate	Product	Time [h]	x [mol %]	y [mol %]	Conv. [%][a]	Yield [%]	d.r.[a]
1	**1b**	**2b**	20	0.1	10	–[b]	–	–
2	**1b**	**2b**	20	10	10	100	60	95:5
3	**1c**	**2c**	6	1	10	100	57	95:5
4	**1d**	**2d**	2	0.1	10	100	90	–
5[d]	**1e**	**2e**	24	0.1	5	100	70	50:50
6	**1f**	**2f**/**2f′**	22	0.1	10	100[c]	74	63:37
7	**1g**	**2g**	60	0.1	10	28	n.d.	n.d.
8[d]	**1h**	**2h**/**2h′**	24	0.1	5	100	60	58:42
9[d]	**1i**	**2i**/**2i′**	24	0.1	5	100	54	58:42

[a] Estimated by ^{1}H NMR spectroscopic analysis. [b] Complex mixture. [c] 53 % conversion without gold. [d] Reaction carried out without inert atmosphere in crude toluene.

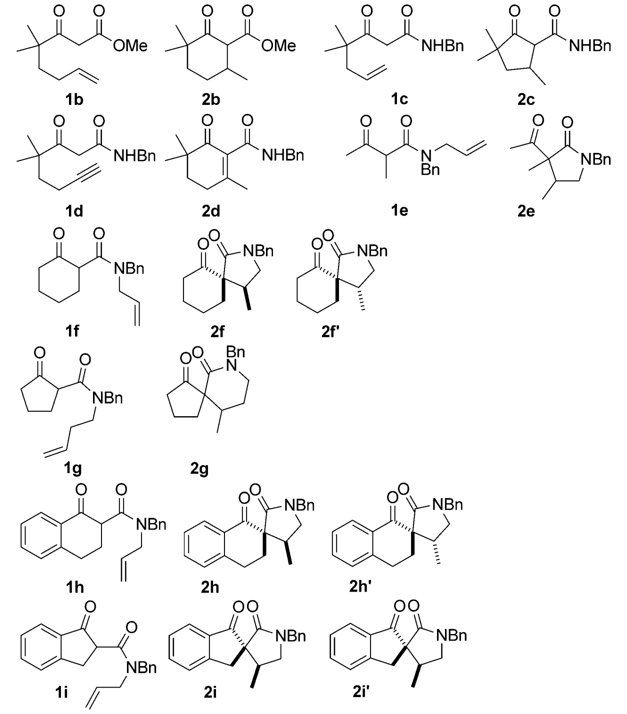
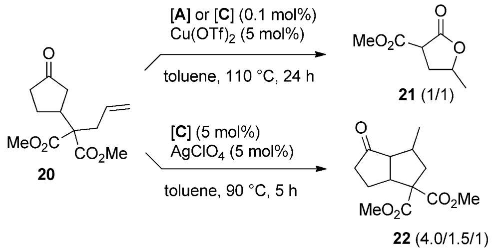


Figure 2. Substrates and products of the Au^{I}/Cu^{II}-catalyzed intramolecular hydroalkylation of β-ketoesters and β-ketoamides.

As mentioned in our preliminary communication, the diastereomeric ratio evolves with time to give the thermodynamic product as the major component. The ratios that are indicated in the table are those obtained at the moment of the recording. In contrast to the ene-β-ketoamide **1 a**, ene-β-ketoester **1 b** decomposed when only 0.1 mol % gold was used (Table 4, entry 1). To encourage its cyclization, the reaction was next carried out with 10 mol % gold, which indeed proved to be a beneficial issue because full conversion into **2 b** was reached (entry 2). Ketoamide **1 c**, which contains one carbon less than **1 a**, transformed into the expected 5-*exo*-trig cyclization product in the presence of 1 mol % gold (entry 3). The Conia-ene reaction[25] of **1 d** was also successfully conducted with 0.1 mol % gold (entry 4). It is worth noting that such addition of β-ketoamides to alkynes have rarely been described and were limited to N-phenyl and $N(alkyl)_2$ substituted substrates.[26] α-Substituted β-ketoamides **1 e–i** were also tested (entries 5–9) and it was found that, with the exception of **1 g** for which the 6-*exo*-trig cyclization proved particularly slow, the 5-*exo*-trig products **2 e**, **2 f**/**2 f**′, **2 h**/**2 h**′, and **2 i**/**2 i**′ formed steadily using 0.1 mol % gold.[27]

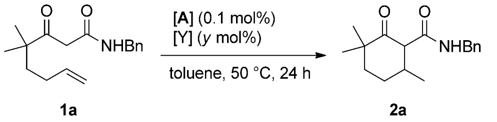
Although the Au/Cu mixture proved versatile and superior to the Au/Ag system in hydroalkylations of unactivated olefins with β-dicarbonyls, we noticed a limitation with α-ketones (Scheme 6). Using either [(JohnPhos)AuCl] (**A**) or [(IPr)AuCl] (**C**) and $Cu(OTf)_2$ as catalytic mixtures with compound **20** gave rise to lactone **21** (full conversion), presumably after retro-Michael and cyclization of dimethyl 2-allylmalonate.[28] On the other hand, the cyclization of **20** into **22** has been described with a Au/Ag system.[24c] The reason why a different product is obtained with the Au/Cu system can be partially explained by the fact that $Cu(OTf)_2$ alone catalyses the formation of **21**, although in the absence of gold only 43 % conversion is reached under these experimental conditions.



Scheme 6. Distinct behavior between the Au/Cu and Au/Ag systems.

It may be argued that triflic acid could play a significant role in the formation of **21** or in the other experiments described above.[29] Although in our preliminary communication,[6] it was shown that the observed reactivity could not be attributed to triflic acid when a gold complex and $Cu(OTf)_2$ were employed, we tried to gain further insight into this aspect of the reaction by using other metal triflates and a selection of chlorides (Table 5). As mentioned above (see Table 1, entry 6), the transformation of **1 a** into **2 a** could be carried out in toluene at 110 °C by using 0.1 mol % [(JohnPhos)AuCl] (**A**) and 10 mol % $Cu(OTf)_2$. The Lewis acids displayed in Table 5 were tested in the absence of gold at 110 °C, which showed that $Ga(OTf)_3$, $Al(OTf)_3$, $Bi(OTf)_3$, and especially $In(OTf)_3$ are potent catalysts (see conversions in parentheses, 12, 16, 38, and 77 % respectively).[30–32] On the other hand, at 50 °C, none of these Lewis

Table 5. Gold(I)-catalyzed intramolecular hydroalkylation of ene-β-ketoamide **1 a** by using various two-component systems.



Entry	[Y]	*y* [mol %]	Conv. [%][a,b]	d.r.[a]
1	$Sc(OTf)_3$	10	0 (0)	–
2	$Yb(OTf)_3$	10	0 (0)	–
3	$Zn(OTf)_2$	10	83 (0)	73:27
4	$Al(OTf)_3$	10	26 (16)	72:28
5	$AlCl_3$	10	0 (0)	–
6	$Ga(OTf)_3$	10	traces (12)	n.d.
7	$GaCl_3$	10	0 (0)	–
8	$In(OTf)_3$	10	100 (77)	74:26
9	$In(OTf)_3$	1	100	73:27
10	Me_3SiOTf	10	100 (0)	73:27
11	$Bi(OTf)_3$	10	100 (38)	72:28
12	$Bi(OTf)_3$	1	100	72:28
13	TfOH	1	0	–
14	TfOH	10	0	–

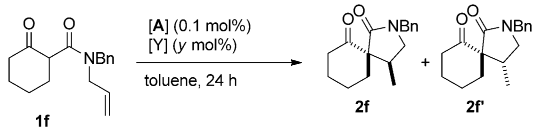
[a] Estimated by ^{1}H NMR spectroscopic analysis; 100 % conversion corresponds to 80 % isolated yield; diastereomeric ratios shown are *trans*/*cis*. [b] Conversions obtained when the reaction was conducted at 110 °C without gold are given in parentheses (no conversion without gold at 50 °C with any additive).

acids promoted the transformation of **1a** into **2a**. By keeping the temperature at 50 °C, the introduction of 0.1 mol% **A** triggered the reaction. Whereas 83% conversion was obtained with $Zn(OTf)_2$ (entry 3), full conversion was reached with $In(OTf)_3$, Me_3SiOTf, and $Bi(OTf)_3$ (entries 8, 10, and 11). These results speak in favor of a synergistic effect between two impotent catalysts to generate an active species (e.g., cationic gold as in the case of $Cu(OTf)_2$) rather than the intervention of triflic acid, unless gold catalyzes the hydrolysis of some metal triflates and not others. Either way, TfOH could not catalyze the reaction, even when using 10 mol% (entries 13 and 14). The reason why metal chlorides are inactive here (compare entries 4/5 and 6/7) could be due to the ability of the triflate anion to serve as a proton shuttle during the catalytic process.[33]

The set of examples described herein shows that the required loading of copper depends on the reaction type and can be as low as 1 mol%. This is not the case for the transformation of **1a** into **2a**. As shown before,[6] the reduction of $Cu(OTf)_2$ loading from 10 to 5 mol% results in a significant increase in the required reaction time. Nevertheless, we noticed that in the case of $In(OTf)_3$ and $Bi(OTf)_3$, only 1 mol% could be engaged (entries 9 and 12), which represents a significant improvement.

With substrate **1f**, it was not possible to reach full conversion with 0.1 mol% **A** and 1 mol% $In(OTf)_3$ or $Bi(OTf)_3$ (Table 6).

Table 6. In^{III}- and Bi^{III}-assisted gold(I)-catalyzed intramolecular hydroalkylation of ene-β-ketoamide **1f**.



Entry	[Y]	y [mol%]	Temp. [°C]	Conv. [%][a]	d.r.[a]
1	$In(OTf)_3$	1	110	62	64:36
2	$In(OTf)_3$	2	110	100	72:28
3	$In(OTf)_3$	5	110	100	76:24
4	$In(OTf)_3$	5	50	100	68:32
5	$Bi(OTf)_3$	1	110	32	59:41
6	$Bi(OTf)_3$	2	110	50	62:38
7	$Bi(OTf)_3$	5	110	100	53:47
8	$Bi(OTf)_3$	5	50	100	56:44

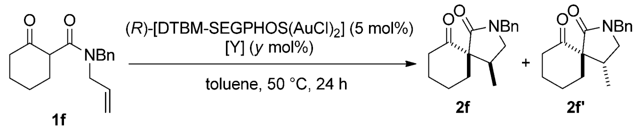
[a] Estimated by chiral SFC; 100% conversion corresponds to 80% isolated yield; diastereomeric ratios shown are **2f**/**2f′**.

At 110 °C, at least 2 mol% $In(OTf)_3$ or 5 mol% $Bi(OTf)_3$ were required (entries 3 and 7). However, the reaction was still possible at 50 °C (entries 4 and 8).

Finally, hydroalkylation of **1f** was carried out by using the digold complex (*R*)-[DTBM-SEGPHOS$(AuCl)_2$] with indium and bismuth activators (Table 7). Whereas no reaction took place with the gold complex alone, the spiro compounds were obtained in enantioenriched form after addition of $In(OTf)_3$ or $Bi(OTf)_3$ (entries 1–4).

Although we have not optimized this reaction, these results clearly rule out the sole participation of TfOH (or gold clusters) in the catalytic process. Indium(III) triflimidate was also tested and proved to be as equally selective as $In(OTf)_3$ (entries 5 and 6).[34] Similar selectivity was obtained with AgOTf (entry 7), which further supports the hypothesis of a common active species in each case.

Table 7. Enantioselective hydroalkylation of ene-β-ketoamide **1f** by using the Au/In and Au/Bi systems.



Entry	[Y]	y [mol%]	Conv. [%][a]	d.r.[a]	ee [%][a,b]
1	$In(OTf)_3$	5	99	71:29	64 (37)
2	$In(OTf)_3$	10	100	61:39	63 (29)
3	$Bi(OTf)_3$	5	78	72:28	66 (38)
4	$Bi(OTf)_3$	10	97	71:29	64 (38)
5	$In(NTf_2)_3$	5	100	67:33	62 (23)
6	$In(NTf_2)_3$	10	100	60:40	63 (24)
7	AgOTf	5	99	78:22	65 (50)

[a] Estimated by chiral SFC; diastereomeric ratios shown are **2f**/**2f′**. [b] The *ee* of the minor diastereoisomer **2f′** is given in parentheses.

Conclusion

This study has revealed that species that are active for a variety of transformations can be obtained from stable [LAuCl] complexes and activators that do not belong to the silver salts family. Typical Au^I-catalyzed reactions are performed by using derivatives of Cu^I, Cu^{II}, Zn^{II}, In^{III}, Si^{IV}, Bi^{III}, and other elements. These catalytic systems were successfully used in various reaction media (toluene, 1,2-dichloroethane (DCE), CH_2Cl_2, THF, MeOH, H_2O) at room temperature and higher (up to 120 °C). Three kinds of ligands were used in the [LAuCl] precatalyst: phosphine, phosphite, or NHC. Zinc, molybdenum, and other salts have already been combined with homogeneous gold catalysis, but their role was not to make the gold complex cationic.[35,36] In those reported examples of cooperative catalysis, silver was also present to generate the active cationic gold species (three-component catalytic mixture), or an isolated cationic gold complex was used. There is also one example of an active gold chloride exhibiting a labile ligand [$AuCl(SMe_2)$] being used jointly with metal triflates such as $Ga(OTf)_3$.[37] Our results are distinct in the sense that gold chlorides **A**, **B**, and **C** display strongly coordinating ligands and are therefore not able to catalyze any of the above transformations by themselves. Because the presence of silver in gold-catalyzed synthesis is sometimes an issue, the use of a silver-free single component catalyst (i.e., a cationic gold complex)[38] or a silver-free two component mixture (e.g., a gold hydroxide and a Brønsted acid[39]) are sometimes advisable.[3c] The other practical approach that is proposed here is the use of a silver-free, two-component mixture composed of a stable [LAuCl] complex and a readily available Lewis acid.

Experimental Section

General experimental information

All commercially available reagents were used as received. [JohnPhosAuCl] (**A**) was either purchased from Strem Chemicals or prepared from Me_2S·AuCl (Aldrich) and JohnPhos (Aldrich),[40] complex **B** was prepared from Me_2S·AuCl (Aldrich) and tris(2,4-di-*tert*-butylphenyl)phosphite (Aldrich),[40] complex **C** was purchased from Strem Chemicals, [(*R*)-DTBM-SEGPHOS-$(AuCl)_2$] was prepared from Me_2S·AuCl (Aldrich) and (*R*)-DTBM-SEGPHOS (Aldrich),[41] $Cu(OTf)_2$, $Al(OTf)_3$, $GaCl_3$, $InCl_3$ were purchased from Alfa Aesar, $Zn(OTf)_2$, $In(OTf)_3$, $Bi(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$, TMSOTf, $In(NTf_2)_3$, $AlCl_3$ were purchased from Aldrich, $Ga(OTf)_3$ was purchased from Acros. 1,2-Dichloroethane (DCE), dichloromethane (CH_2Cl_2), and toluene were distilled over calcium hydride. Tetrahydrofuran (THF) was distilled over sodium. Methanol was used without purification. Wet DCE was prepared by shaking DCE with water in a separatory funnel followed by collection of the organic layer. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Flash chromatography (FC) was performed on 40–63 μm silica gel. Visualization was effected with ultraviolet light and/or *p*-anisaldehyde stain. NMR spectra were recorded with AM250, AV300, AV360, or DRX400 MHz Bruker spectrometers. ^1H NMR chemical shifts were referenced to the residual solvent signal; ^{13}C NMR chemical shifts were referenced to the deuterated solvent signal. Multiplicity was defined by DEPT 135 analysis. Data are presented as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, m = multiplet, br = broad), coupling constant *J* (Hz), integration. High-resolution mass spectra were obtained by electrospray ionization with a TOF instrument (MicrOTOFq Bruker spectrometer). *N*-Allylbenzylamine[42] and *N*-benzylbut-3-en-1-amine[43] were prepared by following reported procedures. Compounds **3**,[44] **4**,[45] **5**,[46] **6**,[46] **7**,[40] **8**,[40] **10**,[47] **11**,[48] **13**,[20] **14a**/**14b**,[20] **17a**/**17b**,[21] **18**,[49] **19**,[49] **20**,[24c] **22**,[24c] methyl 2-methyl-3-oxobutanoate,[50] methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate,[51] and methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate,[52] were already described. Compounds **2g** and **21** were only detected by analysis of the crude reaction mixture and not isolated (in particular, **21** is unstable on silica). Characterization data of the new products are provided in the Supporting Information.

Cycloisomerizations

Cycloisomerization of enyne 3 (Table 2, entry 2); representative procedure: A solution of **A** in DCE (0.5 mg mL^{-1}, 140 μL, 0.134 μmol, 0.1 mol%) and $Cu(OTf)_2$ (4.8 mg, 13.4 μmol, 10 mol%) were added to a solution of enyne **3** (30 mg, 0.134 mmol, 1 equiv) in DCE (1 mL). After stirring for 3 h at rt, the mixture was filtered on a pad of Celite (rinsed with CH_2Cl_2) and the solvent was removed under reduced pressure to afford **4** (24 mg, 80%).

Cycloisomerization of arenyne 5 (Scheme 1): A solution of **B** (0.5 mg mL^{-1}, 174 μL, 0.103 μmol, 0.1 mol%) and $Cu(OTf)_2$ (3.6 mg, 10 μmol, 10 mol%) were successively added to a solution of arenyne **5** (30 mg, 0.103 mmol, 1 equiv) in DCE (1 mL). After stirring for 3 h at 80 °C, the mixture was filtered over a pad of Celite (rinsed with CH_2Cl_2) and the solvent was removed under reduced pressure to afford **6** (28.5 mg, 95%).

Cycloisomerization of arylenyne 7 (Scheme 2):

Dry conditions: $Cu(OTf)_2$ (3.4 mg, 0.009 mmol, 10 mol%) and **A** (0.5 mg mL^{-1}, 100 μL, 0.09 μmol, 0.1 mol%) were added to a solution of enyne **7** (30 mg, 0.09 mmol, 1 equiv) in anhydrous dichloroethane (1 mL). The reaction was heated to 80 °C for 18 h, then filtered over a pad of Celite (rinsed with CH_2Cl_2) and the solvent was evaporated. The residue was purified by FC (SiO_2; pentane/EtOAc, 100:0 to 100:4) to afford **8** (20 mg, 67%).

Wet conditions: $Cu(OTf)_2$ (46 mg, 127 μmol, 0.1 equiv) and **A** (0.5 mg mL^{-1}, 140 μL, 1.27 μmol, 0.1 mol%) were added to a solution of enyne **7** (400 mg, 1.27 mmol, 1 equiv) in wet DCE (13 mL). The reaction was heated at 80 °C for 18 h, then the crude material was filtered over a pad of Celite (rinsed with CH_2Cl_2) and the solvent was evaporated. The residue was purified by FC (SiO_2; pentane/EtOAc, 100:0 to 100:4) to afford **9** (287 mg, 69%).

Alkoxycyclization of enyne 10 (Scheme 3): A solution of **A** (0.5 mg mL^{-1}, 58 μL, 0.055 μmol, 0.1 mol%) and $Cu(OTf)_2$ (2 mg, 0.0055 mmol, 0.1 equiv) were added to a solution of enyne **10** (22 mg, 0.055 mmol, 1 equiv) in MeOH (1 mL). The resulting mixture was stirred at 50 °C for 2.5 h and then filtered over a pad of Celite (rinsed with CH_2Cl_2). The solvent was evaporated to afford **11** (15 mg, 66%).

Hydrations, hydroalkylation, hydroaminations, Meyer–Schuster rearrangement

Hydration of alkynes (Table 3); general procedure: In air, $Cu(OTf)_2$ (y mol%), **A** or **C** (x mol%), THF and H_2O (2:1 v/v, $c = 1$ M), and alkyne (1.0 equiv) were charged in a 10 mL reaction tube equipped with a stir bar and the tube was sealed. The reaction was stirred at 120 °C for 16 h, then the reaction mixture was cooled to rt and the solution was analyzed by ^1H NMR spectroscopy by using 4-methoxybenzaldehyde (1.0 equiv) as an internal standard to determine conversion (by comparison with commercial **12**).

Hydroalkylation of 13 (Scheme 4): In air, **13** (190 mg, 1.0 mmol, 1.0 equiv), $Cu(OTf)_2$ (3.6 mg, 10 μmol, 1 mol%), **A** (0.5 mg, 1 μmol, 0.1 mol%), and CH_2Cl_2 (0.5 mL) were charged in a 10 mL reaction tube equipped with a stir bar and the tube was sealed. The reaction was stirred at rt for 24 h, then the reaction mixture was filtered through a pad of Celite (rinsed with CH_2Cl_2) and evaporated to afford the crude product. Purification by FC (SiO_2; cyclohexane/EtOAc 90:10 to 80:20) afforded a mixture of **14a**/**14b** (1.5:1, 120 mg, 63%).

Hydroamination of alkyne 15b (Scheme 4); representative procedure: In air, $Cu(OTf)_2$ (5.4 mg, 15 μmol, 1 mol%), **A** (0.8 mg, 2 μmol, 0.1 mol%), toluene (1.5 mL), 4-ethynylanisole (0.2 mL, 1.54 mmol, 1.0 equiv), and 2,6-diisopropylaniline (0.32 mL, 90%, 1.54 mmol, 1.0 equiv) were charged in a 10 mL reaction tube equipped with a stir bar and the tube was sealed. The reaction was stirred at 50 °C for 16 h, then the reaction mixture was cooled to rt and analyzed by ^1H NMR spectroscopy, which showed 100% conversion into **17b**.

Meyer–Schuster rearrangement of 18 (Scheme 5): In air, **18** (376 mg, 2.15 mmol, 1.0 equiv), $Cu(OTf)_2$ (36 mg, 100 μmol, 5 mol%), **A** (1.1 mg, 2 μmol, 0.1 mol%), MeOH (8.4 mL), and H_2O (1.6 mL) were charged in a 50 mL reaction tube equipped with a stir bar and the tube was sealed. The reaction was stirred at 60 °C for 14 h, then the reaction mixture was concentrated and diluted with Et_2O. The resulting solution was filtered through a pad of Celite (rinsed with Et_2O) and evaporated to afford the crude product. Purification by FC (SiO_2; cyclohexane/EtOAc, 95:5 to 90:10) afforded **19** (313 mg, 83%).

Hydroalkylations

Formation of type 2 products; general procedure: A solution of **1** (1.0 equiv), metal triflate (y mol%), and gold complex (x mol%)

in toluene (c = 0.1 м) was charged in a 10 mL reaction tube equipped with a stir bar and the tube was sealed. The reaction was stirred at the indicated temperature for 24 h, then the reaction mixture was filtered through a pad of Celite (rinsed with CH_2Cl_2) and evaporated to afford the crude product for which conversion and diastereoselectivity were determined by ^{1}H NMR analysis. Purification by FC (SiO_2; cyclohexane/EtOAc) afforded **2**.

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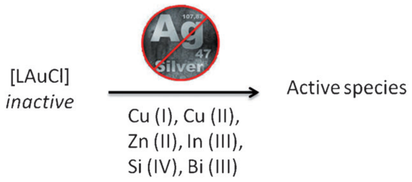
Not just silver: Active gold species have been generated from the corresponding inactive chlorides by using Lewis acids that are not typical in gold chemistry (see figure). Instead of silver salts, complexes of Cu, Zn, In, Si, Bi, and others have been used. This study shows that silver salts, which can cause deactivation processes and side reactions, can be replaced by various activators. Thus, the use of a sensitive cationic gold complex can be avoided.



Gold Catalysis

W. Fang, M. Presset, A. Guérinot, C. Bour, S. Bezzenine-Lafollée, V. Gandon**

■■ – ■■

Silver-Free Two-Component Approach in Gold Catalysis: Activation of [LAuCl] Complexes with Derivatives of Copper, Zinc, Indium, Bismuth, and other Lewis Acids