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Lewis Acid Enhancement of Gold Catalytic Activity Through Counterion Coordination. Synthesis of Benzofulvenes from Progargylsilanes and Benzophenones

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Abstract: A simple, regioselective and high yielding gold-catalyzed synthesis of benzofulvenes, from progargylsilanes and benzophenones, is described. Initially, the carbonyl compound is synergistically activated by the silyl moiety and, for the cyclization step, the gold catalytic activity is clearly increased by the participation of aluminum trichloride, acting as a cocatalyst. Several mechanistic intermediates, such as enynes and silylbenzofulvenes, have been isolated. Different control experiments have been performed, indicating the participation of [LAu][NTf_2AlCl_3] complex as the true catalyst, and revealing a dramatic enhancement of the gold activity by coordination of the Lewis acid to the gold counterion.

Keywords: Gold; Homogeneous catalysis; Lewis acids; Anions; Synthetic methods

Introduction

In the continuous quest for simple methodology for the access to complex structures, homogeneous gold catalysis has become a powerful tool in the last decades.[1] In this field, we have recently performed several gold-catalyzed alkynylations[2] or propargylations[3] of carbonyl compounds using alkynyl or propargylsilanes, respectively. For gold-catalyzed propargylations we were able to demonstrate, through its isolation, the participation of a σ-gold allenyl intermediate[3a] (Figure 1; *top*). In addition, a one-pot synthesis of *trans*-2-silyl-3,4-dihydrofurans could be achieved.[3b] However, we were not able to cyclize homopropargyl silyl ethers starting from aromatic ketones.

On the other hand, several attempts of combination of a gold catalyst with a Lewis acid have been performed, in order to observe a cooperative effect.[4] In this field, just a few examples have been reported further away from independent participation of both species either in a tandem reaction mechanism[5] or

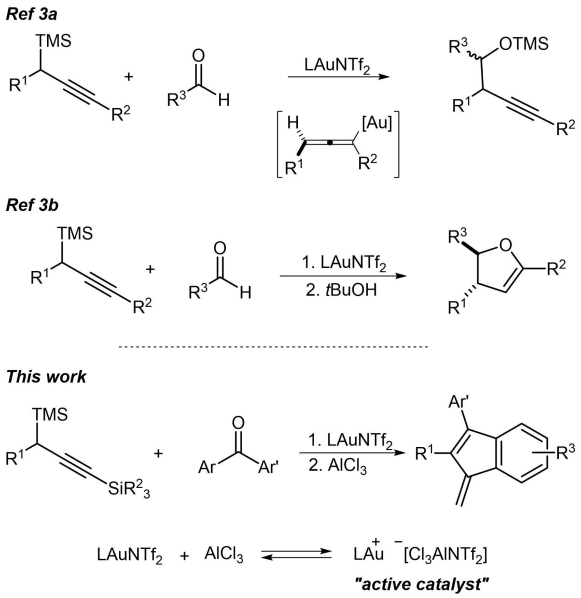


Figure 1. Propargylsilanes in gold-catalyzed propargylations.

facilitating the reaction of the gold intermediate.[6] To the best of our knowledge, participation of Lewis acid as cocatalyst in combination with gold complexes has only been described for activation of non-competent gold catalysts,[7] acting as "in situ" slow and reversible halide exchangers, instead of the commonly used silver salts, to avoid silver interferences[8] or fast halide abstraction, increasing gold decomposition. However, no observations have been reported to date involving enhancement of the gold catalytic activity due to coordination of the Lewis acid to the gold counterion.

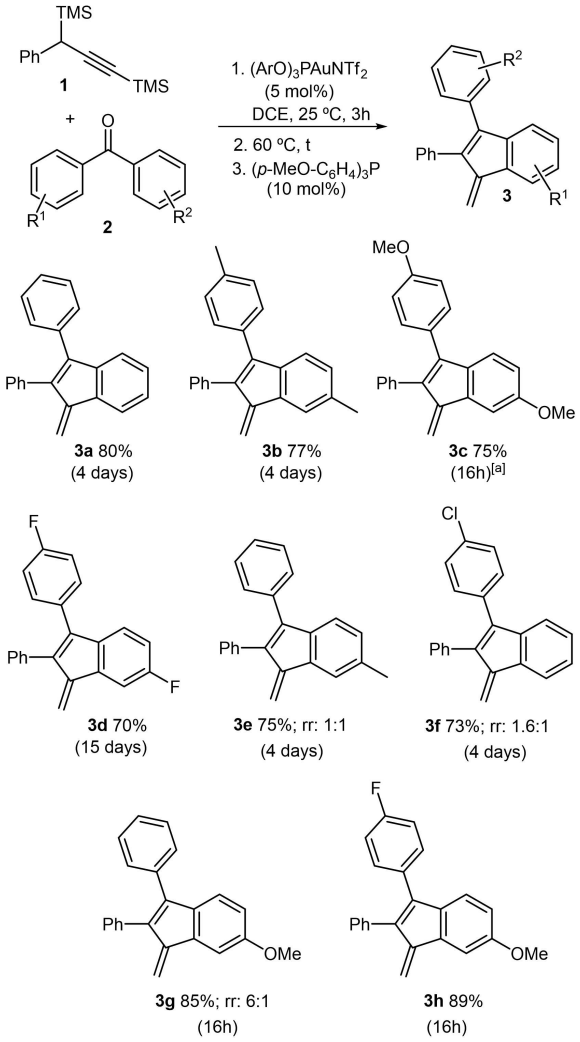
Here we report a novel gold(I)-catalyzed synthesis of benzofulvene derivatives[9] in a one-pot procedure from propargylsilanes and aromatic ketones. In this procedure, gold activity is substantially enhanced by the participation of a low-cost Lewis acid catalyst, such as aluminum trichloride (Figure 1; *bottom*). After a detailed NMR-study of different potentially catalytic species this enhancement could be attributed to Lewis acid coordination to gold counterion.

Results and Discussion

In our initial approach, 1,2-dichoroethane (DCE) solutions of benzophenone derivatives **2** were subjected to a synergistic gold-catalyzed propargylation[3] with three equivalents of 3-phenyl-1,3-bis(trimethylsilyl)-1-propyne **1** followed by a heating period. We observed formation of benzofulvenes **3**, in high yield (Scheme 1). Tris(2,4-di-*tert*-butylphenyl)phosphite was chosen as gold ligand and bis(trifluoromethanesulfonyl)imidate as counterion, following our previously reported methodology.[3] Also, tris-*p*-anisylphosphine [(*p*-$MeOC_6H_4)_3P$] was added, at the end of the reaction, to inactivate the gold catalyst and avoid decomposition issues.

As it is described in Scheme 1, benzofulvenes **3** were obtained from benzophenone and also from benzophenone derivatives bearing electron-donating (**3 b,c**) or electron-withdrawing groups (**3 d**). In addition, the use of non-symmetrical benzophenones, gave rise to the corresponding benzofulvenes **3 e–h** in a regioselective ratio closely related to the electronic nature of the two arene rings. Major isomers, which are represented in Scheme 1, emerged from the cyclization through the electron-richer arene ring. In fact, benzofulvene **3 h** was regioselectively obtained as a single isomer, starting from a benzophenone bearing electron-donating and electron-withdrawing groups in respective arene rings.

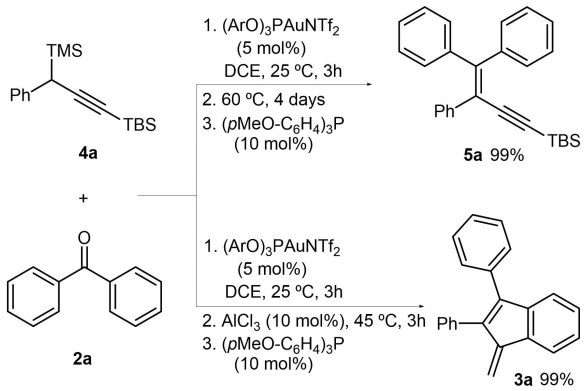
However, reaction times were a major drawback for this transformation, as several days of reaction are required to furnish benzofulvene synthesis, in most cases. In addition, three equivalents of propargylsilane **1** were used due to its decomposition in the reaction course. In this sense, we tried to overcome this issue replacing trimethylsilyl (TMS) group by a more stable



Scheme 1. Synthesis of benzofulvenes **3** through gold-catalyzed propargylation of benzophenone derivatives **2**. Ar = tris(2,4-di-*t*-butylphenyl). [a] Reaction performed at 25 °C.

tert-butydimethylsilyl (TBS) group (compound **4 a**). When the reaction was performed using a single equivalent of propargylsilane **4 a** and under similar reaction conditions, enyne **5 a** was obtained as the only product (Scheme 2). However, to our delight, we observed that the addition, after the propargylation step, of a 10 mol% of aluminum trichloride,[10] gave rise to the formation of benzofulvene **3 a** under milder reaction conditions, much shorter reaction time and quantitative yield.

After the observation of the remarkable effect of the aluminum chloride, we explored this transformation employing other Lewis acids to compare their potential effectiveness. For this study, the reaction was performed under milder conditions (25 °C, in methylene dichloride) and shorter reaction times (1 h) to be able to compare their activity. Two main observations can be highlighted from the results reported in Table 1,



Scheme 2. Preliminary results.

as follows: i) $AlCl_3$ can be considered as the best cocatalyst and ii) the reactivity increases following a good trend with Lewis acidity for comparable compounds (entries 7–10).

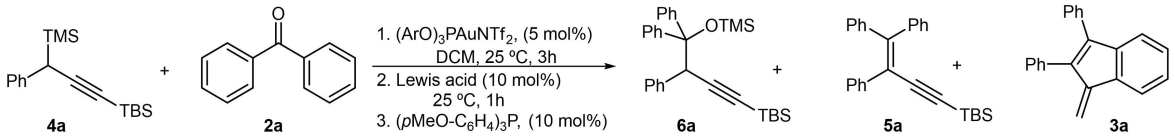
Following this methodology, we next explored the scope of the reaction in terms of substitution pattern and regioselectivity (Scheme 3). As a relevant example, benzofulvene **3 d** was obtained in 16 hours instead of 15 days (*see* Scheme 1). Otherwise, the use of a Lewis acid does not affect to the regioselectivity of the reaction as benzofulvenes **3 e**–**3 h** were obtained with the previously observed regioselective ratio.

Due to the observation of the formation of enyne **5 a** in the course of our research (Table 1), we focussed our efforts to isolate several enynes **5** from the reaction course, under milder reaction conditions, to, in a second stage, reactivate the process to the final formation of benzofulvenes, in order to identify enynes **5** as reaction intermediates. Thus, enynes **5 a,i,g,h** were isolated in high yield lowering the temperature and shortening the reaction times (Scheme 4).

Next, when enynes **5 a,i,g,h** were subjected to the standard reaction conditions, benzofulvenes **3 a,i,g,h**[11] were obtained in high yield (Scheme 5). Additionally, regioselectivity for the reaction of formation of benzofulvenes **3 g,h** was in agreement with the one observed for the one-pot synthesis described in Schemes 1 and 3, (*see above*). These results allow us to identify enynes **5** as truly reaction intermediates. In addition, the use of other enynes, not accessible through the gold-catalyzed propargylation methodology[12] gave rise to the formation of benzofulvenes **9**, with R^3 = aryl (**9 a**), alkyl (**9 b**) or a more robust silyl derivative, as triisopropylsilyl (TIPS) (**9 c**). These results permit to locate the silyl group into the corresponding benzofulvene intermediate.[13] Finally, it is worth to mention that neither the synthesis of enynes **5**[14] nor their reaction to form benzofulvenes **3,9** was observed, under comparable reaction conditions, in absence of $AlCl_3$ or the gold catalyst, indicating a close relationship between both species.

As the next step, we tried to clarify the role of aluminum chloride in the formation of benzofulvenes **3,9**. Initially, from a room temperature one-to-one mixture of aluminum trichloride and bistriflimidate gold(I) complex in CD_2Cl_2, we observed (Figure 2) the

Table 1. Lewis acid screening.



Entry	Lewis acid	**6 a** [%][a]	**5 a** [%][a]	**3 a** [%][a]	Entry	Lewis acid	**6 a** [%][a]	**5 a** [%][a]	**3 a** [%][a]
1	None	99	–	–	6	$Cu(OTf)_2$	–	81	14
2	$Yb(OTf)_3$	99	–	–	7	$InCl_3$	–	86	11
3	$Zn(OTf)_2$	52	47	–	8	$GaCl_3$	–	60	32
4	$Sc(OTf)_3$	20	74	< 5	9	$AlCl_3$	–	50	49
5	$Ga(OTf)_3$	13	82	< 5	10	$AlBr_3$	–	89	10

[a] Yield calculated by ^{1}H-NMR, using dibromomethane as internal standard.

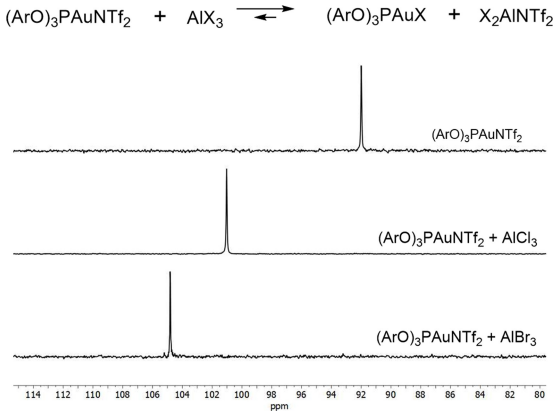
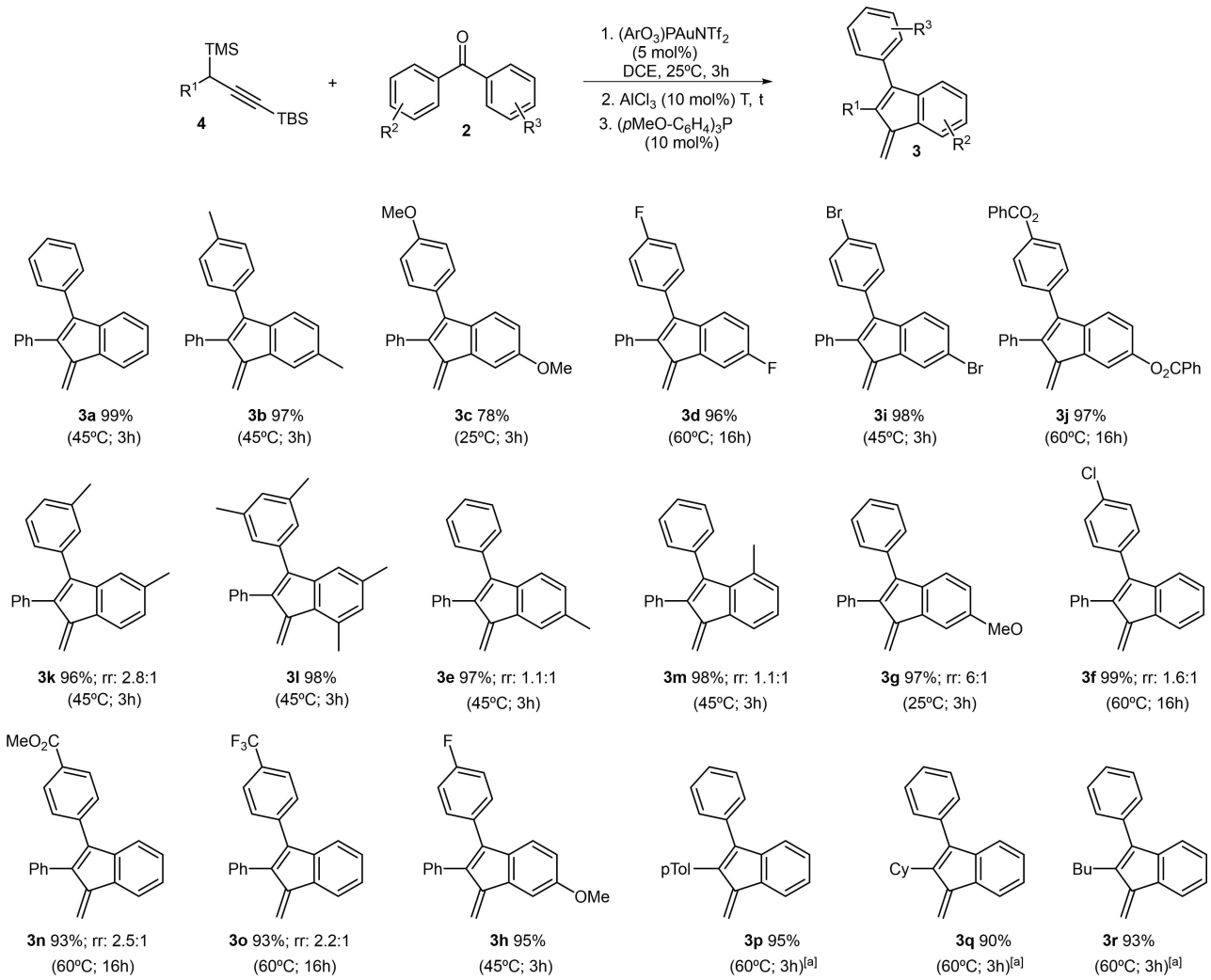
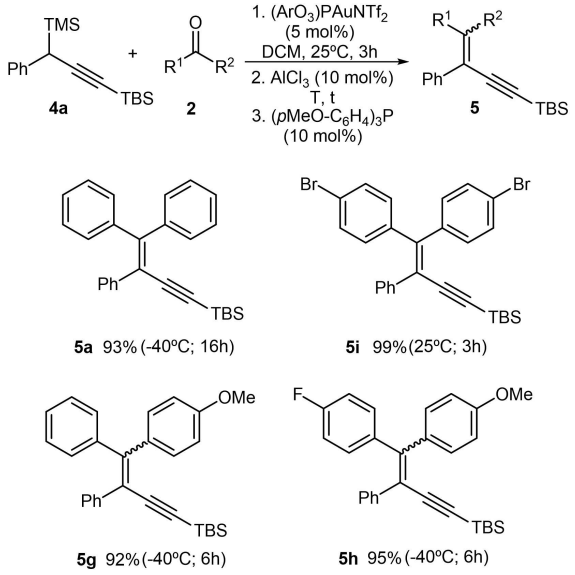


Figure 2. ^{31}P-NMR spectra of several gold complexes (121 MHz; CD_2Cl_2, 25 °C).



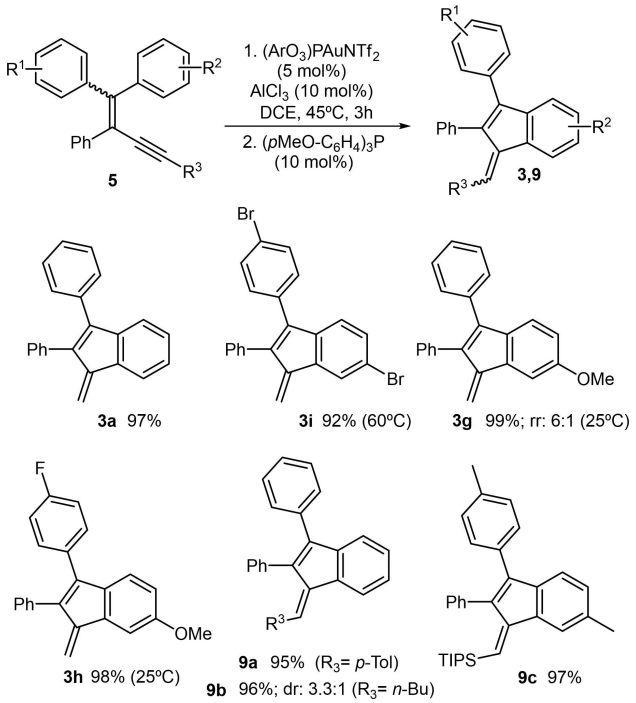
Scheme 3. Scope of the reaction. [a] 60 °C required for propargylation step.



Scheme 4. Capture of enynes **5**.

formation of a new species with a ^{31}P-NMR signal, corresponding to the phosphite ligand, at 101.0 ppm, a significate downfield displacement from 92.0 ppm that belongs to the bistriflimidate gold(I) complex. Similarly, the ^{19}F-NMR displacement of the anion shifted from −76.0 ppm for NTf_2^- to −74.5 ppm, in the new complex. This new species was identified as the corresponding gold(I) chloride complex indicating a highly displaced equilibrium to the gold chloride complex,[15] generating Cl_2AlNTf_2 as by-product.[16] A similar outcome was observed using $AlBr_3$, as the phosphorous signal shifted to 104.8 ppm belonging to the gold(I) bromide complex.[17]

In order to elucidate the nature of the catalytically active species, we performed a set of control experiments. We focused our study on the elimination and cycloisomerization steps,[10] starting from the two types of alkynes, homopropargyl silyl ether **6a** or enyne **5a**, respectively (Table 2). All the reactions were performed in methylene chloride, at 25 °C, and quenched,



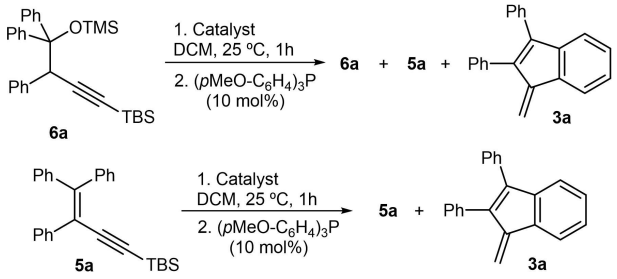
Scheme 5. Benzofulvene synthesis from enynes **5**.

after 1 h, with tris-*p*-anisylphosphine. Experiments with $(ArO)_3PAuNTf_2$ and aluminum trichloride were also performed to serve as reference. In this sense, the use of 10 mol% of $AlCl_3$ (Entry 1) corresponds to the standard reaction conditions, but shorter reaction time, and the moderate lowering of the yield using 5 mol% of $AlCl_3$ (Entry 2) indicates a possible equilibrium between both isolated catalysts and the new active species.

From Table 2 can be inferred that aluminum trichloride does not promote the reaction (Entry 3). Also, exclusive proton catalysis performed by triflimide ($HNTf_2$) –that could potentially appear in the reaction course – can be discarded, as $HNTf_2$ promoted benzofulvene **3a** formation in very low yields (Entry 4). In addition, even lower activity was observed using Cl_2AlNTf_2 in absence of gold(I) complex (Entry 5). On the other hand, gold chloride complex alone behaved, as expected, as a catalytically inactive species (Entry 6) and in the presence of $AlCl_3$ but no triflimide component (Entry 7) very low yield of benzofulvene **3a** was obtained. However, to our delight, the use of a mixture of $(ArO)_3PAuCl$ and Cl_2AlNTf_2 gave rise to a quantitative formation of benzofulvene **3a** (Entry 8).

All these control experiments proved that, for any of the four species involved in the observed equilibrium (Figure 2), independent fully competent catalytic activity was not observed. As the result of this, a complementary equilibrium involving coordination of the Lewis acid to the bistriflimidate counterion (NTf_2^-)

Table 2. Control experiments.



	Catalyst	Alk.	**6a** [%]	**5a** [%]	**3a** [%]
	$(ArO)_3PAuNTf_2$ (5 mol%)	**6a**	–	–	99
1	+ $AlCl_3$ (10 mol%)	**5a**		–	99
	$(ArO)_3PAuNTf_2$ (5 mol%)	**6a**	65	27	7[a]
2	+ $AlCl_3$ (5 mol%)	**5a**		37	60
	$AlCl_3$ (10 mol%)	**6a**	99	–	–
3		**5a**		99	–
	$HNTf_2$ (2.5 mol%)[b]	**6a**	–	84	15
4		**5a**		72	27
	Cl_2AlNTf_2 (5 mol%)	**6a**	68	28	–
5		**5a**		90	7
	$(ArO)_3PAuCl$ (5 mol%)	**6a**	99	–	–
6		**5a**		99	–
7	$(ArO)_3PAuCl$(5 mol%)	**6a**	72	22	< 5
	+ $AlCl_3$ (5 mol%)	**5a**		91	7
8	$(ArO)_3PAuCl$(5 mol%)	**6a**	–	33	65
	+ Cl_2AlNTf_2 (5 mol%)	**5a**		–	99

Yield calculated by ^{1}H-NMR, using dibromomethane as internal standard.
[a] 45% after three hours at 45 °C.
[b] The use of 5 mol% of $HNTf_2$ resulted in decomposition products.

could also be proposed (Figure 3). Participation of this species **10** could explain the reactivity enhancement by lowering the coordination capability of the anion and increasing the electrophilicity of the gold complex.[18] This behaviour would differ from the usually reported gold chloride activations,[7] since a simple anion metathesis could not explain the experimental results summarized in Table 2.

At this point, we focused our efforts in giving experimental support to our hypothesis of participation of complex **10** as the true catalyst. Pursuing this target, a number of low temperature (−85 °C) NMR-experiments were performed, using stoichiometric amounts of enyne **5s** (Figures 4 and 5), bearing a robust

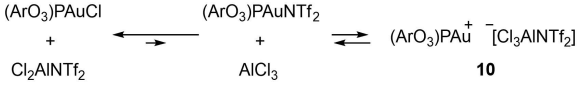


Figure 3. Working hypothesis for the formation of the catalytically active species **10**.

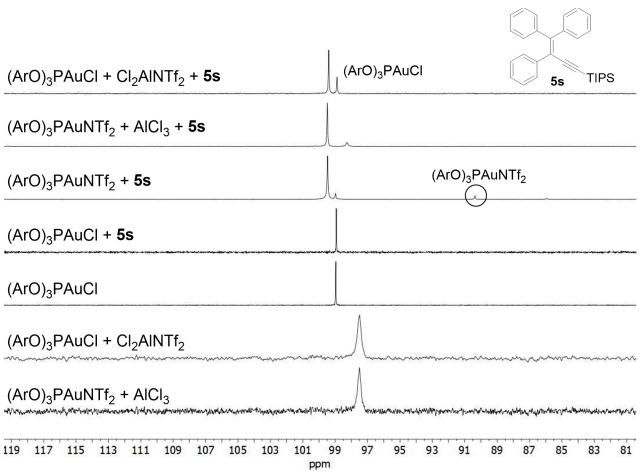


Figure 4. ^{31}P-NMR spectra at −85 °C. (162 MHz; CD_2Cl_2).

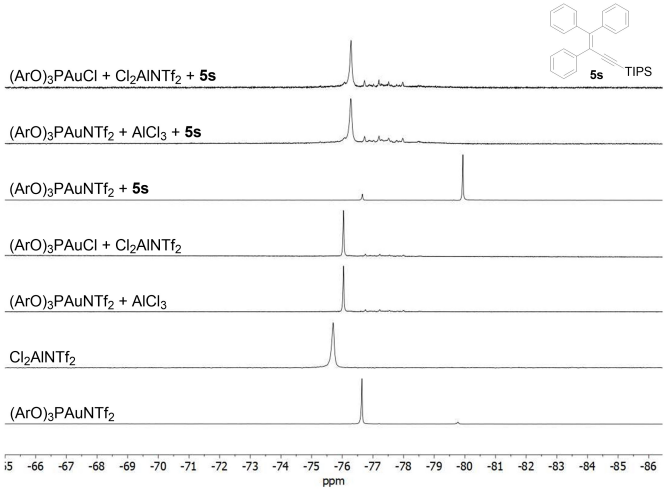


Figure 5. ^{19}F-NMR spectra at −85 °C. (376 MHz; CD_2Cl_2).

triisopropylsilyl group, as the starting material. Initially, complex $(ArO)_3PAuCl$ and mixtures $(ArO)_3PAuNTf_2 + AlCl_3$ and $(ArO)_3PAuCl + Cl_2AlNTf_2$ were dissolved, in CD_2Cl_2 at room temperature, and analysed by NMR at −85 °C. From these experiments we observed that mixtures $(ArO)_3PAuNTf_2 + AlCl_3$ and $(ArO)_3PAuCl + Cl_2AlNTf_2$ exhibited the same ^{31}P-NMR signal (97.5 ppm) that clearly differs from the ones corresponding to free $(ArO)_3PAuCl$ (99.0 ppm) or $(ArO)_3PAuNTf_2$ (90.5 ppm) (Figure 4). Phosphorous signal at 97.5 ppm could correspond to the catalytically active species, not observed at room temperature (Figure 2). On the other hand, same coincidence was also observed in the ^{19}F-NMR spectra (−76.0 ppm) for both combined gold-aluminum species (Figure 5). These results are in agreement with the equilibrium described in Figure 3, and the new species could correspond to complex **10**.

Next, enyne **5s** was added to the different mixtures and the result analysed by ^{31}P, ^{19}F and ^{13}C-NMR at −85 °C. Same signal (99.5 ppm) was observed in the ^{31}P-NMR spectra, for the enyne **5s** coordination of the mixtures $(ArO)_3PAuNTf_2 + AlCl_3$ and $(ArO)_3PAuCl + Cl_2AlNTf_2$ and also for the coordinated $(ArO)_3PAuNTf_2$, indicating the same nature of the cationic units (Figure 4). To our delight, the ^{19}F-NMR spectra reveals the presence of the same signal (−76.3 ppm) for both gold-aluminum mixtures, indicating the presence of the same anion, and importantly differs with the one observed for the complex $(ArO)_3PAuNTf_2$ in the absence of $AlCl_3$ (−80.0 ppm), revealing significant differences in the anion nature (Figure 5). These results are in agreement with our hypothesis of a Lewis acid coordination to the counterion of the gold complex and formation of the catalytically active species **10**.[19] In addition, no coordination of $(ArO)_3PAuCl$ to the enyne **5s** was observed which also agrees with the absence of catalysis using that gold complex.

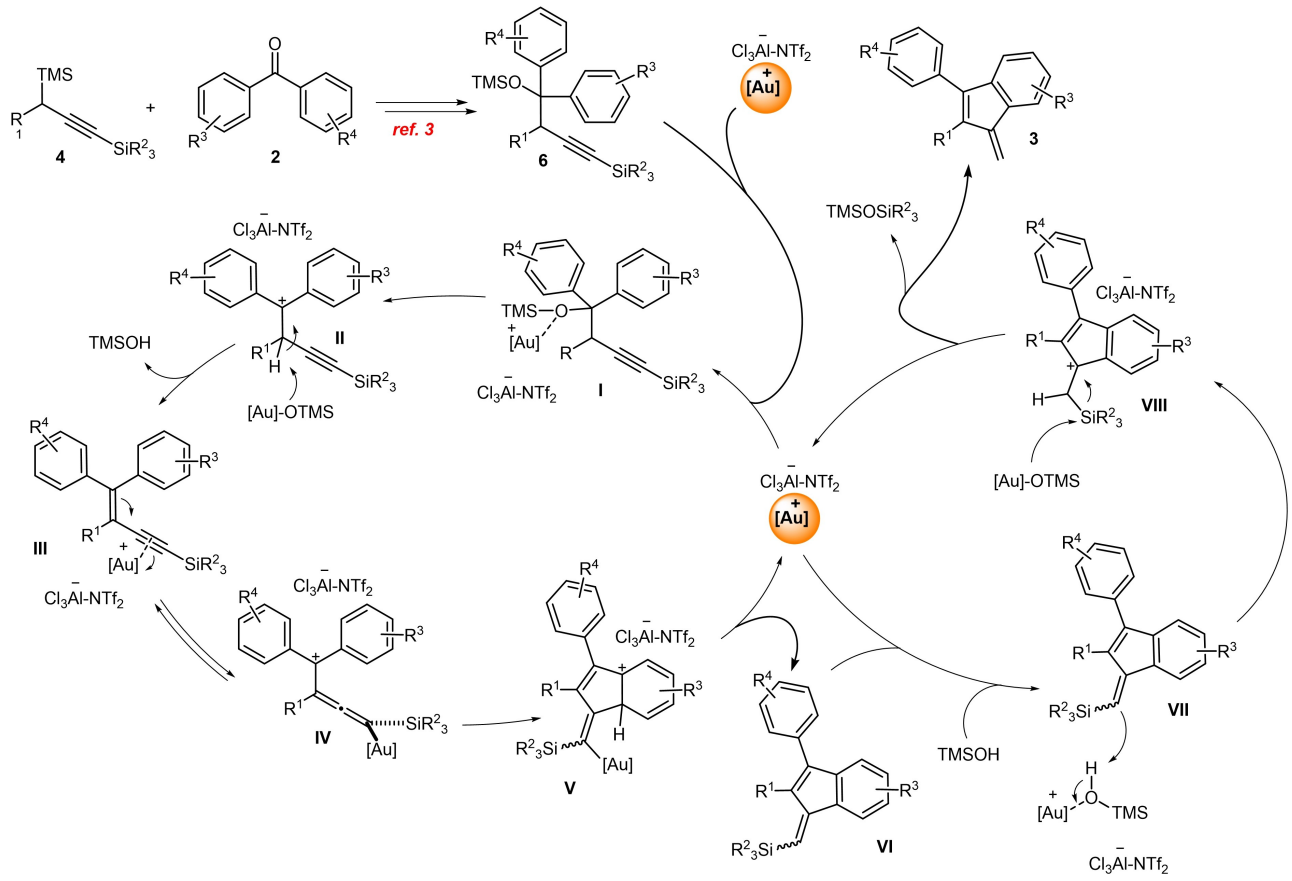
Finally, ^{13}C-NMR spectra of $(ArO)_3PAuNTf2 + AlCl_3$, (ArO)3PAuCl + $Cl_2AlNTf2$ and $(ArO)_3PAuCl$, in the presence of enyne **5s**, are also in agreement with our hypothesis (*See supporting information*).

With all these results in hand, a mechanistic proposal that implies the participation of species **10** could be envisioned and it is outlined in Scheme 6.

Thus, after formation of homopropargyl trimethylsilyl ether **6**, through a synergistic gold-catalyzed propargylation of benzophenone derivative,[3] aluminum trichloride is added and the new highly electrophilic gold complex **10** is formed. This species could coordinate to oxygen atom facilitating the transformation of intermediate **I** into cationic intermediate **II**. Next, hydrogen abstraction, with formation of trimethylsilanol, could lead to enyne intermediate **III**. At this point, equilibrium between enyne **III** and allene **IV** intermediates could occur,[20] allowing free rotation of the single bond, which should explain the regioselectivity of the reaction in terms of the differences in nucleophilicity between the two arene rings. Cationic gold allenyl intermediate **IV** could next experiment ring-closure through a Nazarov-type reaction,[21] leading to formation of benzofulvene skeleton **V**. From intermediate **V**, consecutive rearomatization and protodeauration steps could give rise to silyl benzofulvene intermediate **VI**. Finally, benzofulvene **3** could emerge from a protodesilylation step, with participation of the previously eliminated trimethylsilanol.

Conclusion

In summary, we report here a synergistic gold(I)-catalyzed benzophenone propargylation leading to a wide range of benzofulvene derivatives. As an important breakthrough, the use of a Lewis acid, such



Scheme 6. Mechanistic proposal.

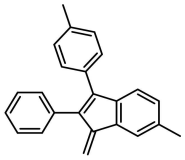
as aluminum trichloride, dramatically increased the gold(I) catalytic activity. Supported by the performance of several control experiments, this remarkable effect can be assigned to Lewis acid coordination to the gold complex counterion. In fact, it can be considered that, for this reaction, aluminum chloride is able to reduce the coordination capability of the counterion, triggering an increment in the electrophilicity of the catalyst, without significantly affecting the stability of the complex. In our opinion, new gold-catalyzed strategies, as activation of low-reactive compounds or enantioselective approaches with chiral Lewis acids, could arise from these results.

Experimental Section

Synthesis of Benzofulvenes 3 from Benzophenones 2

In absence of aluminun trichloride: To a mixture of 0.60 mmol of propargylsilane **1** and 0.20 mmol of benzophenone **2**, prepared in dry 1,2-dichloroethane (1 mL) at 25 °C and under argon atmosphere, 11.2 mg (0,01 mmol, 5 mol%) of tris(2,4-di-*t*-butylphenyl)phosphitegold(I) triflimidate were added and the reaction stirred at 60 °C for the period described in Scheme 1. Finally, 7.0 mg of (pMeO-C_6H_4)$_3$P (0.02 mmol, 10 mol%) were added to deactivate gold catalyst and solvent removed under vacuum. The residue was purified under flash chromatography yielding the corresponding benzofulvenes **3**.

Cocatalyzed by gold(I) and aluminum chloride: To a dry 1,2-dichloroethane solution (1 mL), under argon atmosphere at 25 °C, 0.24 mmol (0,72 mmol for **3c**) of propargylsilane **4**, 0.20 mmol of benzophenone **2** and 11.2 mg (0,01 mmol, 5 mol%) of gold catalyst were added. The mixture was stirred for 3 hours. Next, 2.6 mg (0.02 mmol, 10 mol%) of aluminum trichloride were added and the mixture stirred under the conditions described in Scheme 2. Finally, 7.0 mg of (p-MeO-C_6H_4)$_3$P (0.02 mmol, 10 mol%) were added and the solvent was removed under vacuum. After purification through a chromatographic column, corresponding benzofulvenes **3** were obtained.

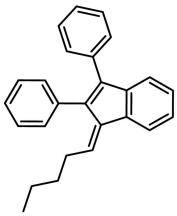


6-Methyl-1-methylene-2-phenyl-3-(p–tolyl)-1*H*-indene (3b): Yield: 77%, 47 mg (from propargylsilane **1**) 97%, 60 mg. (from propargylsilane **4**) Bright yellow solid. *(Slightly decomposes on exposure to air and no melting point can be measured).* R_f (SiO_2) = 0.21 (Hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) = 7.55 (d, J(H,H) = 1.7 Hz, 1H), 7.42-7.19 (m, 8H), 7.19-7.07 (m, 3H), 6.21 (s, 1H), 5.68 (s, 1H), 2.46 (s, 3H), 2.36 (s, 3H). ^{13}C

NMR (75 MHz, $CDCl_3$) δ(ppm) = 147.8 (C), 141.9 (C), 140.4 (C), 137.2 (C), 136.7 (C), 136.5 (C), 135.6 (C), 135.1 (C), 131.8 (C), 130.9 (2×CH), 129.4 (2×CH), 129.1 (2×CH), 128.9 (CH), 128.1 (2×CH), 126.9 (CH), 120.8 (CH), 120.0 (CH), 113.4 (CH_2), 21.7 (CH_3), 21.5 (CH_3). HRMS for $C_{24}H_{20}$ [M]: Calc.: 308.1560; found: 308.1559.

Synthesis of Benzofulvenes 3 or 9 from Enynes 5

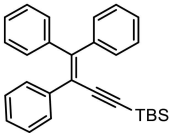
To a mixture of 0.20 mmol of 1,3-enyne **5** in dry 1,2-dichloroethane (1 mL) 11.2 mg (0,01 mmol, 5 mol%) of the gold catalyst were added and the reaction stirred under the conditions described in Scheme 4. Next, 7.0 mg of (p-MeO-C_6H_4)$_3$P (0.02 mmol, 10 mol%) were added and the solvent was removed under vacuum. The residue was purified under flash chromatography, yielding the corresponding benzofulvenes **3** or **9**.



1-Pentylidene-2,3-diphenyl-1H-indene (9b): Yield: 96%, 65 mg ((3.3:1) mixture diasteresoisomers). Bright yellow oil. R_f (SiO_2) = 0.10 (Hexanes/ Ethyl acetate, (100:1)). ^{1}H NMR (300 MHz, $CDCl_3$) *(Major diastereoisomer)* δ(ppm) = 7.91 (m, 1H), 7.53-6.96 (m, 13H), 6.34 (t, J(H,H) = 7.5 Hz, 1H), 2.91 (q, J(H,H) = 7.5 Hz, 2H), 1.77-1.56 (m, 2H), 1.56-1.42 (m, 2H), 1.01 (t, J(H,H) = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *(Major diastereoisomer)* δ(ppm) = 143.5 (C), 140.4 (C), 139.6 (C), 139.2 (CH), 138.7 (C), 135.4 (C), 135.2 (C), 135.0 (C), 131.2 (2×CH), 129.6 (2×CH), 128.1 (2×CH), 127.8 (2×CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 125.3 (CH), 123.7 (CH), 120.2 (CH), 31.7 (CH_2), 29.7 (CH_2), 22.8 (CH_2), 14.0 (CH_3). HRMS for $C_{26}H_{24}$ [M]: Calc.: 336.1873; found: 336.1874.

Synthesis of 1,3-Enynes 5 from Propargylsilanes 4a and Benzophenones 2

To a mixture of 0.24 mmol of propargylsilane **4a** and 0.2 mmol of benzophenone **2** in dry dichloromethane (1 mL) at 25 °C, were added 11.2 mg of the gold catalyst (2.5 mol%) and the reaction was then stirred for 3 hours. After that time, the mixture was was cooled to −40 °C (for **5a,g,h**) and 2.6 mg (0.02 mmol, 10 mol%) of aluminum trichloride were added. The mixture was stirred for 3 h (for **5i**), 6 h (for **5g,h**) 16 h (for **5a**). Finally, 7.0 mg of (p-MeO-C_6H_4)$_3$P (0.02 mmol, 10 mol%) and the solvent was removed under vacuum. The residue was purified under flash chromatography furnishing the corresponding enynes **5**.



***Tert*-butyldimethyl(3,4,4-triphenylbut-3-en-1-yn-1-yl)silane (5a)**: Yield: 93%, 73 mg. White solid; m.p. = 83.4-85.4 °C. R_f (SiO_2) = 0.19 (Hexanes/ Ethyl acetate, (200:1)). ^{1}H NMR (300 MHz, CD_2Cl_2) δ(ppm) = 7.56–7.48 (m, 2H), 7.42-7.27 (m, 5H), 7.23-7.12 (m, 6H), 7.04–6.96 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2) 150.3 (C), 143.0 (C), 141.8 (C), 139.9 (C), 131.3 (2×CH), 130.6 (2×CH), 130.4 (2×CH), 128.3 (2×CH), 128.2 (2×CH), 128.1 (CH), 128.1 (2×CH), 127.7 (CH), 127.4 (CH), 122.0 (C), 108.1 (C), 97.4 (C), 26.2 (3×CH_3), 17.0 (C), −4.7 (2×CH_3). HRMS for $C_{28}H_{31}Si$ [M + H]: Calc.: 395.2190; found: 395.2195.

Experimental Preparation of the Samples for the Low Temperature NMR Experiments of [Tris(2,4-di-tert-Butylphenyl)]Phosphite Gold(I) Triflimidate and Chloride with the Corresponding Aluminum Species

From [Tris(2,4-di-tert-butylphenyl)]phosphite gold(I) bistriflimidate + aluminum chloride: To a solution of 0.05 mmol of triflimide gold complex in 0.5 mL of dry CD_2Cl_2, at 25 °C and under argon atmosphere, 0.05 mmol of $AlCl_3$ (7 mg, 1 equiv.) were added. The mixture was stirred for 30 minutes and analyzed by NMR techniques, under argon atmosphere at −85 °C.

From [Tris(2,4-di-tert-butylphenyl)]phosphite gold(I) chloride + Cl_2AlNTf_2: Under argon atmosphere, to a solution of 0.5 mmol of $EtAlCl_2$ (1 M in hexane), a solution of 0.5 mmol of freshly distilled triflimide (141 mg) in 1 mL of dry CD_2Cl_2 was added dropwise at 0 °C. The cooling bath was removed after complete addition, and the mixture was stirred for 30 min at room temperature, affording a 0.3 M solution of Cl_2AlNTf_2. In a separate Schlenck under argon atmosphere, 0.05 mmol of the corresponding gold chloride complex (44 mg) was dissolved in 0.5 mL of dry CH_2Cl_2, and then 1 equivalent of the previously prepared Cl_2AlNTf_2 solution of (165 µL, 0.05 mmol) was added. Finally, the sample was analyzed by NMR techniques, under argon atmosphere at −85 °C.

Experimental Preparation of the Samples for the low Temperature NMR Experiments of the Different Gold(I) Species and 1,3-Enyne 5s

Following the above procedure, different solutions of 0.05 mmol of each of the gold-aluminum mixtures in 0.5 mL of dry CD_2Cl_2, at 25 °C and under Argon atmosphere, were prepared and cooled down to −85 °C. Then, 0.05 mmol of 1,3-enyne **5s** (22 mg, 1 equiv.) were added, and the mixture was transferred under argon atmosphere and measured by NMR techniques at −85 °C. Similarly, different solutions of 0.05 mmol of the gold(I) triflimide (56 mg) or chloride (44 mg) and 0.05 mmol of enyne **5s** (22 mg, 1 equiv.) were prepared.

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[10] Involvement of $AlCl_3$ in the propargylation step inhibited the reaction.

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[13] Stereochemistry for single (**9a**,**c**) or major (**9b**) diastereoisomers were elucidated by NOE experiments.

[14] A 33% of enyne **5a** was observed, starting from homopropagylsilane **6a**, after 15 h of reaction at 60 °C. Quantitative formation of **5a** requires 65 h.

[15] For similar observation using $Cu(TfO)_2$ as additive: Ref. 7b.

[16] ^{19}F-NMR signal (-74.5 ppm) of this species was in agreement with the one observed for independently synthesized Cl_2AlNTf_2.

[17] Three equivalents of acetonitrile were added to avoid decomposition. Independently, [tris(2,4-di-*tert*-butylphenyl)phosphite]gold(I) bromide, was synthesized from the corresponding gold-chloride complex, for comparison.

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