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Intermolecular [2 + 2] Cycloaddition of Alkyne-Alkene Catalyzed by Au(I) Complexes. What Are the Catalytic Sites Involved?

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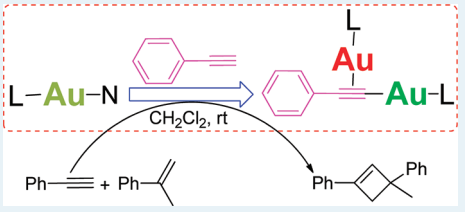
Supporting Information

ABSTRACT: Bulky Au(I) biphenylphosphine complexes form with phenylacetylene isolable digold complexes under conditions of the room-temperature intermolecular [2 + 2] cycloaddition of phenylacetylene and α-methylstyrene. Single-crystal X-ray diffraction (XRD) of two digold complexes show the presence of Au atoms connected to the C≡C triple bond of a phenylacetylene subunit through a σ and a π bond. The two Au atoms are fluxional and undergo exchange even at −80 °C. These digold complexes exhibit as catalysts almost complete selectivity toward the intermolecular cycloaddition and higher final yield to the corresponding cyclobutene than the corresponding mono Au(I) complex precursor. The difference in selectivity between the commercial mono Au(I) complex and the corresponding digold-phenylacetylene complex was found to be due to the generation of Brönsted acids of the counteranion [$HSbF_6$ or $HN(CF_3SO_2)_2$ in the cases studied] that are formed by replacement of the C≡C−H by a C≡C−Au bond. This Brönsted acid causes α-methylstyrene dimerization and degradation of the cyclobutene, two processes that do not occur when the reaction is promoted by the digold complex.



KEYWORDS: homogeneous gold catalysis, cycloaddition reaction, diaurate complex as catalyst, Au(I) complex as precatalyst

INTRODUCTION

Gold catalysis is currently a hot topic in homogeneous and heterogeneous catalysis aimed at delineating the specific properties of gold with respect to other noble metals.[1] Gold(I) complexes are well-known catalysts to activate C=C[2,3] and C≡C multiple bonds.[4−11] The generally accepted mechanism of C≡C triple bond activation is by interaction of Au^+ with the C≡C π cloud. This assumption is supported by single crystal X-ray diffraction (XRD) characterization of Au(I)/C≡C complexes.[12,13]

Recently it has been reported that terminal alkynes react with aromatic alkenes through an intermolecular [2 + 2] cycloaddition promoted by positive Au(I) phosphine complexes.[14] It was proposed that the reaction mechanism is "*consistent with a reaction of cationic Au(I)-alkyne complexes with the alkenes to form*" Au(I)-carbene cyclopopyl-like intermediates.[14]

For the intermolecular [2 + 2] cycloaddition catalyzed by cationic Au(I) it was reasoned "that inactivation of the catalyst by the alkenes and competitive pathways could be minimized by using sterically hindered cationic Au(I) complexes that could selectively activate alkynes in the presence of alkenes".[14] Concerning selectivity of the cycloaddition with respect to alkene it was also observed experimentally that the Au(I) phosphine catalysts exhibit low selectivity, and consequently 100% excess of alkene with respect to the alkyne should be used during the reaction to achieve higher conversions toward cycloaddition[14] and, therefore, the reported process was notably unselective from the point of view of the alkene. The lack of alkene selectivity can be surprising considering the preferential activation of alkynes over alkenes by Au(I) catalysts. This fact that Au(I) shows generally a high preference for alkyne activation and that, however, alkenes exhibit high reactivity is an indication that the catalytic process is more complex than just the [2 + 2] cycloaddition and that the reactions taking place cannot be fully explained with the available information. A better understanding of the reaction mechanism and the identity of the active species can lead to more efficient and selective catalysts.

In the present work, we have found that, under the reaction conditions, isolable digold-phenylacetylene adducts are formed (Scheme 1). The formation of digold complexes liberates $HSbF_6$ or $HN(CF_3SO_2)_2$ in the reaction media that are responsible for the low alkene selectivity observed toward [2 + 2] cycloaddition (Scheme 2). Furthermore, it has been observed that the digold complexes when isolated and used as catalysts give almost complete selectivity, though lower activity, than the initial positive Au(I) phosphine complex. Kinetic experiments indicate that the catalytic process probably involves mono and dinuclear gold complexes. While this work was under review, we become aware of a mechanistic study for the cycloisomerization of 1,6-enynes showing that although diaurate complexes of phosphine Au(I) are formed under the conditions they are unlikely to be

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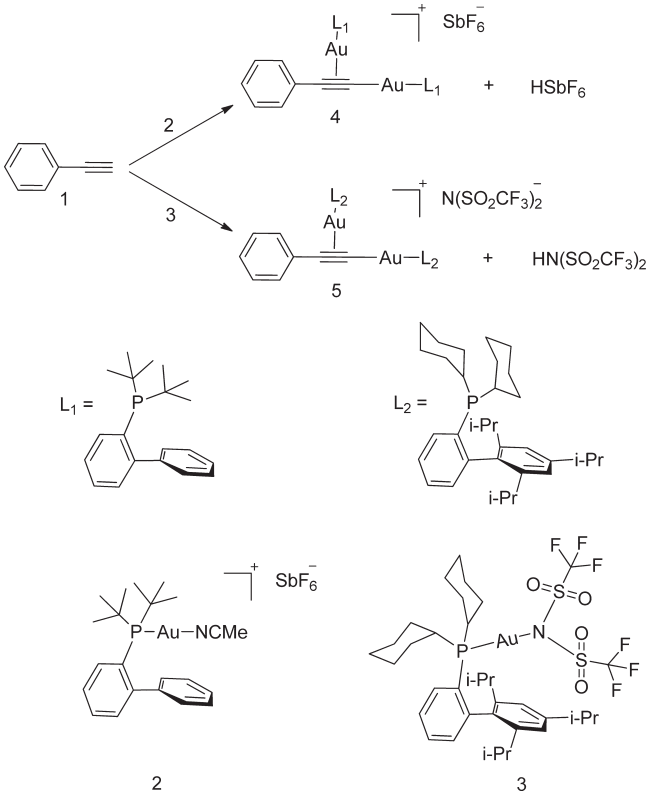
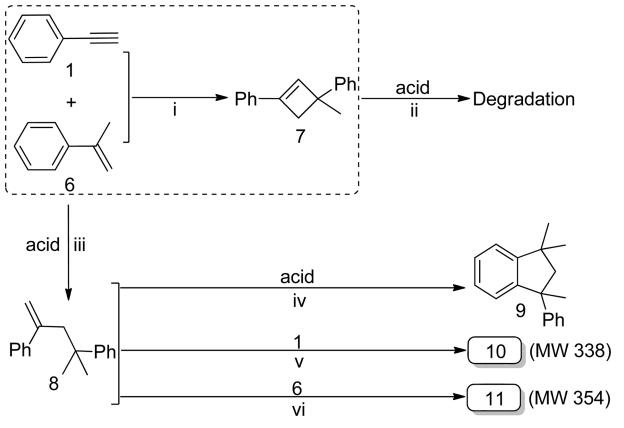
Scheme 1. Synthesis and Structure of Cationic Digold Complexes 4 and 5



Scheme 2. Pathways Occurring Concomitantly to the Intermolecular [2 + 2] Cycloaddition of Phenylacetylene (1) and α-Methylstyrene (6) Catalyzed by Gold Complexes[a]



[a] (i) Intermolecular cycloaddition; (ii) degradation of cyclobutene **7** by acids; (iii) dimerization of **6** to the styrene **8**; (iv) cyclization of styrene **8** promoted by acids; (v and vi) consecutive reactions observed for complexes **2** and **3** as consequence of the formation of styrene **8**.

intermediates in the process.[15] We notice, however, that the steric encumbrance of the biphenylphosphine ligand studied here and the Ph-Au interaction present in our complex can play a role making the behavior of our complex different from that of simple triphenylphosphine ligands.

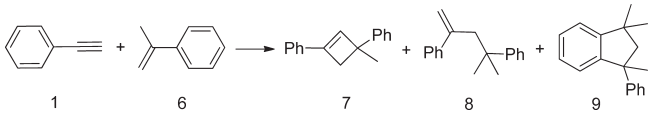
RESULTS AND DISCUSSION

A preliminary study was carried out trying to reproduce the results reported in the literature with complex **2**.[14,16] Similar results to those reported were obtained, though with lower yield of cyclobutene **7** because of the consecutive reaction of primary cyclobutene **7** (see Table 1). Table 1 summarizes the results that have been achieved here, and a more complete list of the catalytic results can be found in the Supporting Information, Table S1. Dimerization of α-methylstyrene **6** to form a primary olefinic and a secondary cyclic dimer also takes place simultaneously and explains why a large excess of styrene **6** is required to achieve high alkyne conversions (see Supporting Information, Figure S1). When complex **3**[17,18] was used as catalyst, the reaction proceeded with lower selectivity and lower final yield toward cycloaddition (see Table 1, entry 2 and footnote d). The lower selectivity of complex **3** having $(CF_3SO_2)_2N^-$ as counteranion contrasts with the reported data for the SbF_6^- analogue (complex C in ref 14).

Nature of Catalytic Sites. Isolation of Digold-Phenylacetylene Complexes. It is not uncommon that gold complexes transform/decompose during the catalytic process. Thus, to determine if complexes **2** and **3** remained stable during reaction, the ^{31}P NMR spectra of the alkyne-alkene mixture containing complexes **2** or **3** as catalyst were recorded while reacting. It can be seen in the Supporting Information, Figure S2 that, even at the shortest monitored reaction time (5 min), a single ^{31}P peak at 62.7 ppm for complex **2** is recorded. This peak does not correspond with that of the original complex **2** (57.49 ppm). Analogously, complex **3** evolves to give two new ^{31}P NMR peaks appearing at 44.85 ppm (small) and 38.39 ppm (large) (Supporting Information, Figure S3) that do not correspond with that of the original complex **3** (33.29 ppm). Over the time, the peak at 44.85 ppm decreases even further and eventually completely disappears, while the peak at 38.39 remains. Independent experiments exposing separately phenylacetylene (**1**) or styrene (**6**) to complex **3** clearly show that the peak at 38.39 ppm derives from the interaction of **3** with acetylene **1**, while the peak at 44.85 ppm that eventually disappears is due to the interaction of complex **3** with styrene **6**. This ^{31}P NMR spectroscopic study shows a somewhat different behavior of Au(I) complexes **2** and **3**. While in the presence of alkyne **1** complex **2** does not interact with alkene **6**, complex **3** forms initially an adduct with alkene **6** that finally disappears leading to the exclusive formation of the adduct with alkyne **1**.

The above spectroscopic study shows that the original complexes **2** and **3** introduced as catalysts undergo a certain transformation into other gold species at very early stages of the reaction. Then, in an attempt to find species generated during the course of the reaction that could be catalytically relevant, we isolate two adducts of phenylacetylene (**1**) and Au(I) phosphine complexes (see Scheme 1) by reaction at room temperature for 4 h in CH_2Cl_2 of phenylacetylene with Au(I) complexes **2** and **3** and subsequent solvent evaporation. This treatment afforded colorless crystals of the air-stable cationic digold complexes **4** and **5** in good isolated yields with respect to the initial Au(I) complex (ca. 70−80%) (see Experimental Section). Furthermore, ^{1}H, ^{13}C, and ^{31}P NMR spectra of gold complexes isolated after starting the [2 + 2] cycloaddition indicate that under the reaction conditions the starting complexes **2** and **3** introduced as catalysts were converted into the corresponding complexes **4** and **5** (see Supporting Information, Figures S4−S5 and Figures S6−S8).

Table 1. Results of the Room-Temperature Reaction of 1 and 6 in CH_2Cl_2 Promoted by Different Catalysts



						yield (%)[a]		
entry	catalyst (mol %)	time (h)	conversion (%) **1**	conversion (%) **6**	selectivity (%) **7**	**7**	**8**	**9**
1	**2** (3)	23	82	96[b]	52	43[c]	33[d]	2
2	**3** (3)	24	88	94[b]	26	23	36[e]	
3	**4** (3)	28	89	57[b]	**91**	**81 (75)**	5	
4	**4** (1.5)	26	82	58[b]	**90**	**75**	7	
5	**4** (3)	30	95	97[f]	**92**	**86 (79)**	3	
6	**4** (1.7)[g]	40	96	98[g]	**94**	**89**		
7	**5** (1.4)	90	47	28[b]	**91**	37	4	
8	**4** (1.5)[h] + $HSbF_6$ (4.3)	1	61	97[b]	50	32	62	9
		3	83	98[b]	14	12	4	17

[a] Yields determined by using ^{1}H NMR spectroscopy and GC. The number in brackets correspond to isolated yields. [b] Alkyne/Alkene molar ratio 1:2. [c] Entry 4 in Table 1 of ref 14 reported 67% under the same conditions. [d] 30% of products obtained by reaction of phenylacetylene and α-methylstyrene with **8** with respective molecular ion peak in GC-MS at 338 and 354 amu. [e] Product having a molecular peak in GC-MS of 338 amu and whose ^{1}H NMR spectrum shows a new singlet at 5.85 ppm accompanied by the peak at 6.72 ppm due to compound **7**. [f] Alkyne/Alkene molar ratio 1:1. [g] reused catalyst (recovered from Entry: 5, washed and dried). [h] The catalyst was a combination of Au(I) complex and $HSbF_6$.

After crystallization, colorless crystals of stable cationic digold complexes **4** and **5** were obtained, and their structure could be resolved by single crystal XRD (Figure 1) (Supporting Information, Tables S2 and S3). Further characterization was carried out by liquid ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra and solid state ^{31}P and ^{19}F NMR (see Supporting Information, Figures S9−S14 for complex **4** and Supporting Information, Figures S15−S20 for complex **5**). It is interesting to note that digold complexes **4** and **5** were obtained even at (**2** or **3**)/**1** molar ratios as low as 0.5 mol % where a large excess of phenylacetylene exists and formation of a possible mono adduct of phenylacetylene with the Au(I) complexes versus the isolated digold complex would be favored. The Supporting Information, Figures S21−S23 show the ^{1}H, ^{13}C, and ^{31}P NMR spectra of the reaction mixture at 4 h when an excess of cationic complex **2** over **1** is added to demonstrate that even under these conditions the digold complex **4** is the only detectable species. It should be noted that control ^{1}H NMR experiments in CD_2Cl_2 show that this technique is able to detect the presence of minute amounts of complex **2** in the presence of a large excess of complex **4** by recording two sets of methyl groups at 1.39/1.34 and 1.38/1.33 ppm, corresponding to the *tert*-butyl groups of the diaurate **4** and monoaurate **2** complexes when a 95:5 mixture of these two complexes is monitored at concentrations of 4.1×10^{-3} and 2.1×10^{-4} M, respectively. This detection limit of our ^{1}H NMR spectroscopy indicates that the concentration of monoaurate complex **2** during the catalytic reactions should be below this detection limit. Precedents reporting the formation of digold-acetylene complexes can be found in the literature.[19] Moreover, in the case of cycloisomerization of 1,5-allenynes, "*experimental and computational evidence shows that the ene reaction proceeds through a unique nucleophilic addition of an allene double bond to a cationic phosphinegold(I)-complexed phosphinegold(I) acetylide*".[20] This type of active digold complex was predicted because "the formation of phosphinegold acetylide is very favorable..." and subsequent addition of a second Au(I) complex will lead to a diaurate species. However, digold complexes with biarylphosphine ligands had not been yet isolated.

The crystal structure of complexes **4** and **5**, which are rapidly formed during the course of the reaction, could be resolved by single-crystal XRD (Figure 1). They show the presence of a Au(1)−C(1) σ bond with the respective distances 2.026(8) Å and 2.022(4) Å for complex **4** and **5**, respectively, as well as a η^2 interaction with a second Au(2) atom and the C(1)≡C(2) triple bond with the respective distances 2.198(7) Å, 2.335(6) Å and 2.198(4) Å, 2.308(4) for complexes **4** and **5**, respectively. In addition, complexes **4** and **5** also exhibit a short distance between each gold atom and the corresponding distal phenyl ring of the biphenyl ligand (distance Ct1(C15→C20) to Au1: 3.0021 (0.0059) Å and distance Ct2(C35→C40) to Au2: 3.0521 (0.0055) Å for complex **4** and distance Ct1(C15→C20) to Au1: 3.0754 (0.0029) Å and distance Ct2(C48→C53) to Au2: 3.1644 (0.0023) Å for complex **5**), although this length is somewhat longer than the one that has been estimated by a meaningful interaction between the metal and the phenyl ring (2.95 Å).[21]

The electrospray ionization mass spectrometry (ESI-MS) of a solution obtained after dissolving complex **4** in CH_2Cl_2 / methanol 1/1 shows a positive MS peak at 1091.4 amu that corresponds to the expected mass for the cationic digold complex $[C_{48}H_{59}Au_2P_2]^+$ together with the expected negative MS peaks at 234.6 and 236.6 amu corresponding to the anionic counteranion $[SbF_6]^-$. When ESI-MS of the reaction mixture is monitored it is interesting to note that besides the previously commented peaks corresponding to complex **4**, extra weak peaks whose values match with those of the mono Au(I) adduct with **1** (see Supporting Information, Figure S24) were also recorded. However, no additional spectroscopic evidence of the presence of this mono Au-**1** complex could be obtained.

Analogously, ESI-MS recorded upon dissolving complex **5** shows a peak at 1447.6 amu that agrees with the expected mass for the cationic digold complex $[C_{74}H_{103}Au_2P_2]^+$ together with a

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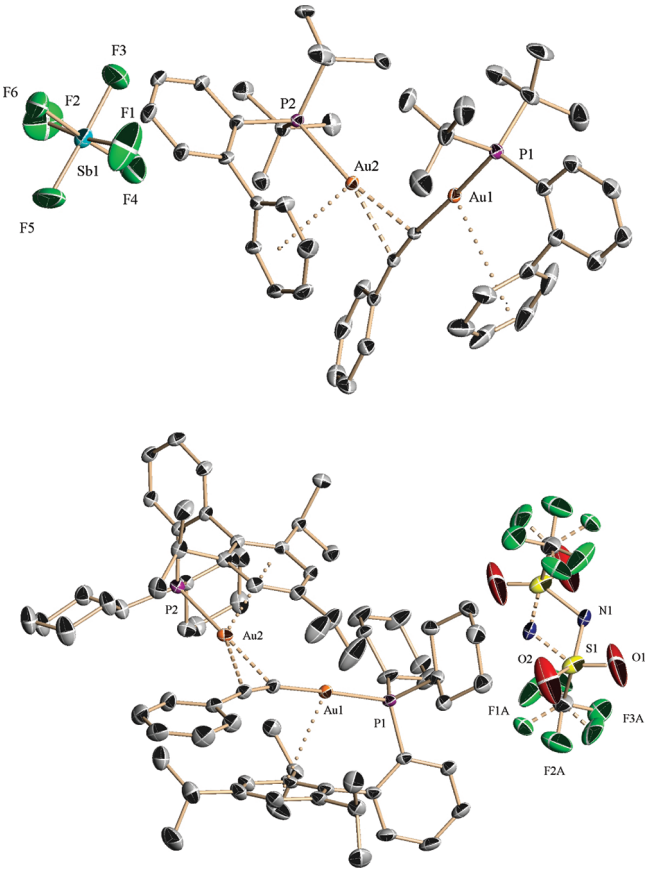

Figure 1. Molecular structure of complexes **4** (top) and **5** (bottom) obtained by single-crystal XRD. Solvent (either CH_2Cl_2 or hexane for **4** and **5**, respectively) and hydrogen atoms are omitted for clarity (see Supporting Information for labeled drawings of compounds **4** and **5**).

peak at 279.8 amu corresponding to the anionic counteranion $[N(SO_2CF_3)_2]^-$. Also in the case of complex **3**, the ESI-MS of the reaction mixture reveals that, in addition to the peaks corresponding to complex **5**, other weaker peaks whose values are compatible with the mass of the mono Au(I) adduct with phenylacetylene **1** were also recorded (see Supporting Information, Figure S25).

A possible rationalization of how complexes **4** and **5** are formed could be as follows: the first gold complex interacts with the C≡C triple bond forming a σ carbon−gold bond of a gold acetylide through cleavage of Au−N and C−H bonds. The mono Au(I) complex σ-bonded to the C≡C bond can probably fluctuate with the η^2 complex with the C≡C triple bond. No mono gold complex could, however, be isolated and, therefore, this hypothesis still remains to be proven. Apparently a second gold complex interacts with the π orbitals of C≡C triple bond, increasing the electrophilicity of this functional group, before the catalysis takes place.

Although single-crystal XRD shows in the solid state the presence of two nonequivalent Au(I) atoms (see Figure 1), these complexes undergo in solution a very fast fluxional exchange between the two Au(I) atoms with respect to the carbon−carbon triple bond of phenylacetylene. This exchange is evidenced in ^{31}P NMR spectroscopy where a single ^{31}P signal appearing at 62.71 and 38.39 ppm for complexes **4** and **5**, respectively, is recorded. The difference in chemical shift for the ^{31}P atoms of complexes **4** and **5** is significant and follows a similar trend as the parent complexes **2** (57.49 ppm) and **3** (33.29 ppm) in deuterated dichloromethane. The characterization of a related cationic digold-alkyne complex has been recently reported in the literature, in which one gold atom is σ bonded to *t*-butylacetylene and a second one exhibits a η^2 interaction with the π cloud of C≡C triple bond.[19] Also in this reported case, in spite of the no equivalence of the two Au(I) atoms, a single peak was observed in ^{31}P NMR spectroscopy even when the temperature is decreased to −80 °C. Also in our case, ^1H and ^{31}P NMR spectra of a CD_2Cl_2 solution of complexes **4** and **5** do not undergo any change upon recording the spectra at −80 °C compared to the spectrum recorded at room temperature except an increase in peak width. However, when ^{31}P spectra of complexes **4** and **5** were recorded in the solid state, we were able to record in both cases two singlets with the same integral corresponding to each distinct σ and π bonded gold phosphine appearing at 61.97 and 61.42 ppm and 41.25 and 39.01 ppm for complexes **4** and **5**, respectively. (See Supporting Information, Figures S13 and S19).

Catalytic Implications of the Formation of Digold Complexes 4 and 5. At this point it appears that since the first moment of the reaction the starting complexes **2** and **3** disappear and the system is not as simple as was initially thought. Besides mono Au(I) complexes, digold complexes **4** and **5** are also present as well as the acid form of the corresponding anion [$HSbF_6$ or $HN(SO_2CF_3)_2$]. Therefore, it becomes mandatory to determine the catalytic activity of the digold complexes **4** and **5** and the $HSbF_6$ or $HN(SO_2CF_3)_2$ acids, as well as their role on the low selectivity observed for the alkene. First of all, and following Scheme 1, it appears that the formation of 1 mol of the digold complexes **4** and **5** implies the liberation of 1 mol of $HSbF_6$ or $(CF_3SO_2)_2NH$. Blank controls indicate that under reaction conditions $HSbF_6$ promotes dimerization of α-methylstyrene **6** to dimers **8** and **9** as previously reported for other Brönsted acids.[22] Similarly $HN(SO_2CF_3)_2$ (10 mol %) catalyzes very efficiently in a short time the transformation of styrene **6** into the cyclic indane. This dimerization is actually observed to a large extent when the [2 + 2] cycloaddition is started using complexes **2** and **3**. Therefore, it is now possible to explain that the low alkene selectivity for cycloaddition was not due to the bulkiness or nature of the starting gold complexes **2** and **3**, but was due to the presence of $HSbF_6$ or $HN(SO_2CF_3)_2$ formed very early during the reaction by the decomposition of some **2** and **3** with the corresponding formation of the digold complexes **4** and **5**.

With respect to the catalytic activity of these digold complexes formed during the reaction, a preliminary experiment clearly established that cationic digold complexes **4** and **5** do not react with α-methylstyrene. This contrasts with the reactivity of styrene **6** promoted by $HSbF_6$ or $HN(SO_2CF_3)_2$ to form styrene dimers (see pathways iii and iv in Scheme 2), something that occurs when starting the reaction with Au(I) complexes **2** and **3**. However, digold complexes **4** and **5** were active and very selective in promoting the room-temperature intermolecular [2 + 2] cycloaddition of **1** and **6** (see Table 1 entries 3 to 7 and in Supporting Information, Figures S26 and S27 for a ^1H and ^{13}C NMR spectra of the reaction mixture at 30 h after removal of complex **4** used as catalyst and evaporation of volatile compounds and compare with the selectivity toward cyclobutene **7** based on the ^1H NMR spectrum of Supporting Information, Figure S1).

Figure 2 compares conversion and selectivity based on reactant **1** for the cycloaddition when the reaction is promoted by complex **2** or complex **4**. Initial reaction rate for the formation of

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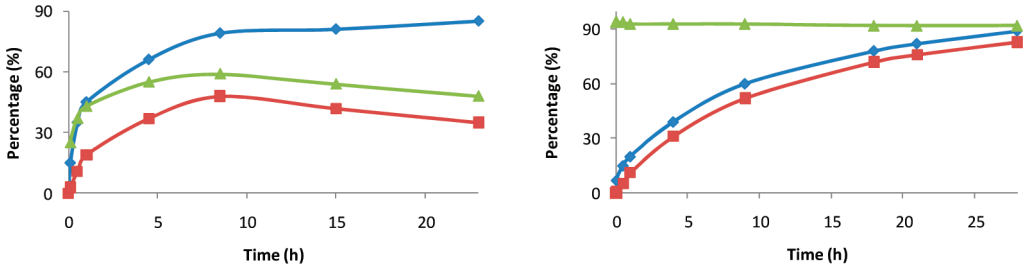

Figure 2. Time/conversion-yield-selectivity plot for the room temperature cycloaddition of **1** and **6** in CH_2Cl_2 in the presence of 3 mol % of complex **2** (left) and **4** (right). Reaction conditions: 1.5 bar of argon and 1:2 alkyne/alkene ratio. Conversion of **1** (◆); selectivity to **7** (▲); and yield of **7** (■).

cyclobutene **7** is similar when starting with complex **2** ($r_o = 3.0 \times 10^{-6}$ mol min^{-1}) or with complex **4** ($r_o = 2.7 \times 10^{-6}$ mol min^{-1}), but the selectivity to cyclobutene **7** is much lower using complex **2** as catalyst than with the digold complex **4**.

The selectivity of alkene **6** to the cyclobutene **7** using digold complex **4** is so remarkable that the reaction can be performed using stoichiometric amounts of **1** and **6** giving a yield to **7** even higher than using complexes **2** or **3** as catalysts (Table 1, entry 5). In addition, complex **4** can be recovered and reused for a consecutive run without deactivation (Table 1, entry 6).

Notice that the selectivity curve indicates that even the cyclobutene product **7** can further react when the reaction is initiated by complex **2**, probably because of the presence of the $HSbF_6$ generated during the course of the transformation of complex **2** into complex **4**. This was confirmed by putting cyclobutene **7** in contact with $HSbF_6$ and observing degradation of compound **7** (see Supporting Information, Figures S28 and S29).

To provide some evidence to the hypothesis that the catalytic behavior of complex **2** can be considered derived from the combination of the activity of complex **4** and $HSbF_6$, an experiment was performed in which 2.8 equivalent amounts of $HSbF_6$ were added on purpose to the reaction with the cationic digold complex **4** and the results obtained practically match those achieved starting with complex **2** (Table 1, entry 8). A similar behavior was observed for the set of complexes **3** and **5**. The above results reveal the undisclosed role of $HSbF_6$ and $(CF_3SO_2)_2NH$ disguising the catalytic behavior of Au(I) complexes. The control experiments showing the activity of $HSbF_6$ and the combination of digold complex **4** and equivalent amounts of $HSbF_6$ clearly reveal the role of the counteranion accompanying the positive Au(I) complexes.

Another important point is to determine if the phenylacetylene unit forming part of the digold complexes **4** and **5** is activated for the intermolecular [2 + 2] cycloaddition. To gain evidence on the reactivity of this phenylacetylene unit a control reaction in which the digold complex **4** was added in stoichiometric amounts to α-methylstyrene **6** was performed. No reaction was observed, and the expected cyclobutene **7** was not formed. This result indicates that phenylacetylene forming part of complex **4** is inert and, therefore, this C≡C triple bond is not activated for the cycloaddition.

Dependence of the Initial Reaction Rate of 7 Formation on the Concentration of Au(I). At this point, we can already conclude that (a) the operating catalytic system is not as simple as was previously assumed,[14] but it evolves during the reaction; (b) that by means of a deeper physicochemical study it was possible to find a catalytic system that gives very high selectivity with respect to alkene and to the cycloaddition product **7**; (c) it appears quite plausible that during the reaction there is an equilibrium between the mono and digold complex, since addition of $HSbF_6$ in stoichiometric amounts to the reaction with complex **4**, reproduces the results with complex **2**; and (d) in situ generated Brönsted acids [$HSbF_6$ or $(CF_3SO_2)_2NH$)] play a role promoting dimerization of alkene **6** and decreasing the stability of cyclobutene **7**.

To get further insight, a study of the initial reaction rates of the [2 + 2] cycloaddition versus the Au(I)/phenylacetylene molar ratio, and versus the diaurate complex **4** (see Figure 3, panels a,c and b,d respectively) allow to calculate the relative rate of the monogold and diaurate complexes when starting with low concentrations of each one of them. The results indicate that the diaurate complex appears to be active to promote the intermolecular cycloaddtion leading to cyclobutene **7**, its activity being about one-half of the activity of the monoaurate complex **2**.

■ CONCLUSIONS

In the present work we have shown that under the reaction conditions reported for the intermolecular [2 + 2] cycloaddition, fluxional digold-complexes with phenylacetylene are formed and can be isolated and characterized from the reaction mixture. Formation of these digold complexes should lead to the generation of stoichiometric amounts of the corresponding conjugated acid of the gold complex counteranion. If this counterion is a poor nucleophile, then, a strong Brönsted acid is generated in the reaction medium promoting the undesirable dimerization of α-methylstyrene and degradation of the cyclobutene **7**. The catalytic activity and selectivity of the positive Au(I) complexes can be understood as a combination of the activity of mono Au(I) and digold-phenylacetyene complex (**4**) and that of the Brönsted acid. In fact the digold complex exhibits much higher selectivity and yield than that of the reported positive Au/complexes. Overall the present work shows the obvious potential of mechanistic studies and isolation of catalytically relevant species to gain control on the selectivity of Au(I) catalyzed reactions.

■ EXPERIMENTAL SECTION

All reactions were carried out under Ar in solvent dried using a Solvent Purification System (SPS).^{1}H NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts of ^{1}H signals are reported in ppm with the solvent resonance as the internal standard (CD_2Cl_2: 5.27 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, sept = septuplet, m = multiplet), coupling constants (Hz) and assignment. $^{13}C\{^1H\}$NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts of ^{13}C are reported in ppm with the solvent resonance as the internal standard (CD_2Cl_2: 53.84 ppm). ^{31}P and ^{19}F NMR spectra were recorded 300 MHz spectrometers. Chemical shifts are reported in ppm.

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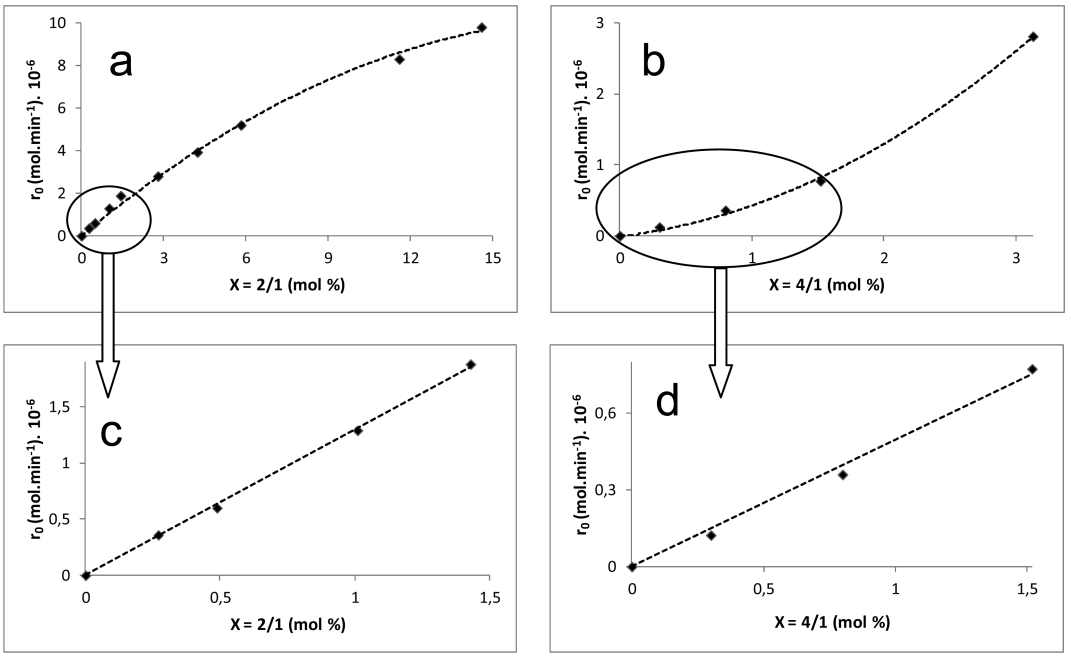

Figure 3. Plot of the initial rate of cyclobutene **7** formation (r_0) vs the **2**/**1** (a and c) and **4**/**1** (b and d) molar percentage (X). Reaction conditions: Alkyne/alkene molar ratio 1:2 in CH_2Cl_2 (1 mL) at room temperature; 1.5 bar of Ar; the amount of complexes **2** and **4** was varied as indicated in the plot.

Gas chromatography (GC) was performed with a Varian 3900 apparatus equipped with an TRB-5MS column (5% polysylarylene, 95% polydimethylsiloxane, 30 m, 0.25 mm ×0.25 μm, Teknokroma). GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated at the same conditions.

ESI-MS were performed on an Agilent Esquire 6000 instrument.

Synthesis of Complex 4 [{Au(L$_1$)}$_2$(CCPh)][SbF$_6$]. Dichloromethane (1.5 mL) was added to a mixture of complex **2** [Au(L$_1$)(NCMe)][SbF$_6$] (0.077 g, 0.1 mmol) and phenylacetylene (**1**) (0.025 g, 0.25 mmol). The solution was stirred at room temperature for 4 h and then the resulting mixture was evaporated to dryness in vacuum. The crude product was washed with cold *n*-hexane (3 × 1 mL) and redissolved in dichloromethane (0.5 mL) and *n*-hexane (∼2 mL) was added until the solution turned muddy; after standing for 15 h at −30 °C, a colorless crystalline material corresponding to complex **4** was obtained. A sample suitable for X-ray crystallography was isolated by filtration, washings with cold *n*-hexane and drying (0.054 g, 72% yield).

Elemental analysis, calculated for $C_{48}H_{59}Au_2F_6P_2Sb\cdot 2CH_2Cl_2$ (%): C, 40.10; H, 4.24. Found: C, 40.19; H, 4.08.

ESI-MS *m*/*z*: 1091.4 amu for $[C_{48}H_{59}Au_2P_2]^+$; 234.6 and 236.6 amu for $[SbF_6]^-$.

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.84 (m, 2 H; ArH); 7.52 (m, 4 H; ArH), 7.41 (m, 5 H; ArH), 7.32−7.18 ppm (m, 8 H; ArH), 7.08−7.05 ppm (m, 4 H; ArH), 1.39 ppm (s, 18 H; CH_3), 1.34 ppm (s, 18 H; CH_3).

^{13}C NMR (CD_2Cl_2): δ = 149.73, 149.55, 143.13, 143.04, 134.32, 133.66, 133.56, 133.11, 131.49, 129.71, 129.44, 129.08, 128.40, 127.81, 125.83, 125.23, 121.29, 116.62, 38.47, 38.15, 31.27, 31.17 ppm. ^{31}P NMR (CD_2Cl_2): δ = 62.71 ppm.

Synthesis of Complex 5 [{Au(L$_2$)}$_2$(CCPh)][N(SO$_2$CF$_3$)$_2$]. Dichloromethane (1.5 mL) was added to a mixture of complex **3** Au(L$_2$)[N(SO$_2$CF$_3$)$_2$] (0.095 g, 0.1 mmol) and phenylacetylene (**1**) (0.025 g, 0.25 mmol). The solution was stirred at room temperature for 4 h and then the resulting mixture was evaporated to dryness in vacuum. The residue was washed with cold *n*-hexane (3 × 1 mL) and redissolved in dichloromethane (0.5 mL). *n*-Hexane (∼ 2 mL) was added until the clear solution turned muddy. After standing for 15 h at −30 °C, colorless crystalline material corresponding to complex **5** was obtained. A sample suitable for X-ray crystallography was isolated by filtration, washings with cold *n*-hexane, and drying (0.066 g, 76% yield).

Elemental analysis, calculated for $C_{76}H_{103}Au_2F_6NO_4P_2S_2$ (%): C, 52.81; H, 6.01; N, 0.81; S, 3.71. Found: C, 52.80; H, 6.18; N, 0.87; S, 3.21.

ESI-MS *m*/*z*: 1447.6 amu for $[C_{74}H_{103}Au_2P_2]^+$; 279.8 amu for $[N(SO_2CF_3)_2]^-$.

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.65−7.56 (m, 2 H; ArH); 7.54−7.46 (m, 4 H; ArH), 7.43−7.28 (m, 5 H; ArH), 7.2−7.1 ppm (m, 2 H; ArH), 6.83 ppm (s, 4 H; ArH), 2.59 ppm (sept, 2 H; i-PrCH), 2.18 ppm (sept, 4 H; i-PrCH), 2.17 ppm (m, 4 H; CyCH); 2.1−1.6 ppm (m, 20 H; $CyCH_2$); 1.45−1.19 ppm (m, 20 H; $CyCH_2$); 1.18 ppm (d, 12 H; i-PrCH$_3$); 1.07 ppm (d, 12 H; i-PrCH$_3$); 0.83 ppm (d, 12 H; i-PrCH$_3$).

^{13}C NMR (CD_2Cl_2): δ = 149.69, 147.29, 147.10, 146.66, 136.05, 135.96, 134.26, 134.15, 133.20, 132.68, 131.38, 130.62, 128.89, 128.12, 128.02, 126.62, 125.93, 121.85, 121.07, 118.21, 38.11, 37.68, 34.41, 31.99, 31.16, 30.86, 27.41, 27.24, 27.14, 26.96, 26.16, 25.75, 24.55, 23.46, 23.06, 14.28 ppm. ^{31}P NMR (CD_2Cl_2): δ = 38.39 ppm.

■ ASSOCIATED CONTENT

Supporting Information. Liquid and solid state NMR spectra, ESI-MS and crystal data of complexes **4** and **5**. Spectroscopic data of the [2 + 2] reaction mixture in the presence of complexes **2** and **3** as starting catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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