Organometallic Gold(III) Compounds as Catalysts for the Addition of Water and Methanol to Terminal Alkynes

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Abstract: Different inorganic and organometallic gold(III) and gold(I) complexes have been tested in the addition of water and methanol to terminal alkynes. Anionic and neutral organometallic gold(III) compounds can efficiently mediate these reactions in neutral media in refluxing methanol. The compounds are added in catalytic amounts (1.6-4.5 mol % with respect to the alkyne). Thus, compounds of the general formula Q[Au(R)Cl]3, Q[Au2R2Cl2], [Au(RCl)2]2, and [Au(R2Cl)2] (Q = BzPPh3+, PPN: N(PPh3)2+ or N(But)4+; R = C8F5 or 2,4,6-(CH3)3C6H2) seem to behave as Lewis acids in nucleophilic additions to triple bonds. Some intermediates could be detected in the stoichiometric reaction between [Au(C6F5)2Cl]2 and phenylacetylene that was followed by variable temperature 1H, 19F, COSY 1H-19F, 1H-1H, and 1H-13C NMR experiments. Compound [Au(C6F5)2Cl]2 is also able to catalyze the hydration of phenylacetylene at room temperature. A plausible mechanism for the hydration reaction has been proposed.

Introduction

The hydration of unactivated alkynes, an abundant hydrocarbon resource, is a safe and environmentally benign route to form C=O bonds. Although the hydration of alkynes can be mediated by acids, it generally requires a large excess of acidic reagent, and only electron-rich acetylene compounds react with high conversions.1 Transition metals have been used to catalyze this process as well as the analogous reaction in which alcohols are added across the triple bond.2 The most extensively employed catalytic systems consist of toxic mercury salts in acidic media,3 but other transition-metal-complex catalysts containing Ru(III),4 Rh,5 Pd(II),6 Pt,7 Cu(II),8 or Ag(I)8 metal centers as well as some Ir–M (M = Pd, Pt) clusters3b have been described. These catalytic systems lead to the obtention of ketones because all known additions of water to alkynes follow Markovnikov’s rule. More recently, Ru(II) complexes, in the presence of appropriate auxiliary phosphate ligands, have efficiently catalyzed the anti-Markovnikov addition of water to terminal alkynes, yielding mainly aldehydes.10 The use of gold compounds in homogeneous catalytic organic reactions has been undervalued for many years due to the preconceived opinion that gold is an expensive and extremely chemically inert metal. However, recent reports have changed this assessment, and gold salts in small amounts are known to display high catalytic activity.11 Gold(III) acids or salts such as HAuCl4, HAuCl4/AgNO3, Na[AuCl4], anhydrous AuCl3, and Au2O3 or gold(I) complexes such as [AuCl2(PPh3)3], [AuCl2(Ph3)2], [AuMe2(PPh3)2], [Au(2,2-diybisdicyclohexylphosphate)], ([Au(PPh3)2]2), and gold(I) compounds with chiral ferrocenylphosphine ligands have behaved as good catalysts for different organic reactions. Thus, asymmetric aldol reactions,12 diboration of vinylarenes,13 dehydrogenative dimerizations of trialkylstannanes,14 carbonylation of olefins15 and amines,16 C–C and C–O bond couplings,18–23

oxidation of sulfides, or, more recently, the selective oxidation of thioethers can be catalyzed or mediated by gold(III) or gold(I) compounds. Gold has been an effective catalyst in the addition of nucleophiles to triple bonds. In 1991, Utimoto et al. described that \( \text{Na[AuCl}_4 \) (2 mol %) could catalyze the addition of water and methanol to terminal and internal alkynes in neutral media. However, the process was not regioselective for nonsymmetric internal alkynes. In 1998, Teles and co-workers reported the addition of methanol to alkynes catalyzed by Au(I) species in conjunction with acidic cocatalysts. More recently, Tanaka et al. have described that Au(I)-acid systems in aqueous methanol serve as useful catalysts which promote the hydration of alkynes and have high turnover frequencies. Nevertheless, the authors did not isolate or identify possible metallic intermediates in these reactions.

We decided to test the catalytic activity of gold(III) organometallic complexes in the addition of water and alcohols to alkynes in neutral media as the incorporation of organic fragments to the gold(III) centers may help to stabilize and to identify possible intermediates by spectroscopic methods. We initiated our studies with gold(III) anionic compounds bearing one or two pentafluoropheny1 (C\textsubscript{6}F\textsubscript{5}) or mesityl (2,4,6-(CH\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) radicals that had been previously described by us. Some of the complexes displayed catalytic activity, and we tested neutral gold(III) inorganic and organometallic compounds as well as gold(I) and gold(II) compounds in the absence of acidic cocatalysts. Some gold(III) and gold(I) organometallic complexes were tested in conjunction with acids. Here, we report the results of these studies as well the identification of some gold(III) intermediates in the stoichiometric additions of phenylacetylene to neutral gold(III) organometallic complexes.

### Results and Discussion

#### 1. Hydration of Phenylacetylene

1.1. Hydration with Gold(III) Complexes. The hydration of phenylacetylene (1) in refluxing aqueous methanol has already been described by Utimoto et al. with the gold(III) salt \( \text{Na[AuCl}_4 \) (2 mol %, 1 h).

Scheme 1 shows the hydration of phenylacetylene (1) to give phenylmethyl ketone (2) in 91 % yield. More recently, Tanaka and co-workers have achieved the hydration of 1 to give 2 in 98 % yield by using the gold(I) catalytic system \([\text{AuMe(PPh}_3]_2\) (0.2 mol %):H\textsubscript{2}SO\textsubscript{4} (50 mol %) in aqueous methanol at 70 °C (1 h).

In our studies, the amount of gold compound used was generally 2 mol % (with respect to the alkynyl), and the reaction was carried out in refluxing methanol over 1 h.30 Utimoto and co-workers reported that the pH of Na[AuCl\textsubscript{4}] in aqueous methanol was slightly acidic (around 5), implying somehow that it was an acid-based catalysis. However, there was preliminary evidence that one of the plausible reaction pathways may be the cleavage of a Au–Cl bond and subsequent coordination of the alkynyl as the first step.

All of the catalytic results are shown in Tables 1 and 2. We studied the hydration of 1 in neutral media (Table 1) and in conjunction with acids (Table 2). The gold(III) compounds chosen were inorganic neutral compounds and anionic and neutral organometallic complexes in which one or more chloride ligands have been replaced by organic groups. Thus, inorganic neutral gold(III) derivatives such as [AuCl\textsubscript{3}(tht)]\textsubscript{3} and [AuCl\textsubscript{3}(PPh\textsubscript{3})]\textsubscript{2} do not give conversion of 1 to 2 or the conversion is very poor (11%). However, anionic organometallic gold(III) complexes of the type Q[AuCl\textsubscript{2}] (Q = BzPPh\textsubscript{3} (benzyl triphenyl phosphonium), R = mes\textsubscript{3} or C\textsubscript{6}F\textsubscript{5}\textsubscript{2}) as well as neutral [AuCl\textsubscript{2}]\textsubscript{2} compounds in which a chloride has been replaced by an organic mononuclear radical behave as good catalysts (Table 1). We chose the mesityl (2,4,6-(CH\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) and pentafluorophenyl (C\textsubscript{6}F\textsubscript{5}) radicals for two main reasons: (a) their electronic and steric properties are quite different (resembling the electronic properties of the C\textsubscript{6}F\textsubscript{5} group as compared to those of a chloride ligand); and (b) our research group has prepared a large variety of gold(I), gold(III), and even gold(II) complexes with these radicals.

Gold(III) organometallic compounds that behave as good catalysts or that we use in subsequent stoichiometric reactions have been numbered in the tables and throughout the text. Neutral complexes were prepared in situ by reaction with silver salts (Scheme 2 and Experimental Section) and loaded in a 4.5 mol % ratio.

Whereas the compound with one mesityl group (4) is not catalytically active (entry 2), the compound with a pentafluorophenyl radical (8) gives 100 % yield in the above-mentioned reaction conditions (entry 4). The reaction is sensitive to the amount of catalyst used (entries 1 and 2).

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32. (The synthesis of BzPPh\textsubscript{3}[Au(C\textsubscript{6}F\textsubscript{5})Cl\textsubscript{2}] is carried out by oxidative addition of PhCl\textsubscript{2}I to BzPPh\textsubscript{3}[Au(C\textsubscript{6}F\textsubscript{5})Cl] in a way similar to that for the obtention of BzPPh\textsubscript{3}[Au(mes)Cl\textsubscript{3}].)
33. (a) [AuCl(tht)]\textsubscript{3} obtained by reaction of [AuCl(tht)]\textsubscript{2} and PhCl\textsubscript{2} (1:1 molar ratio). (b) Uson, R.; Laguna, A.; Vicente, J. J. Organomet. Chem. 1977, 131, 471.
34. [AuCl\textsubscript{3}(PPh\textsubscript{3})] obtained by reaction of [AuCl\textsubscript{3}(PPh\textsubscript{3})]\textsubscript{2} and PhCl\textsubscript{2} (1:1 molar ratio).
Organozinc Gold(I) Complexes as Catalysts

Table 1. Hydration of Phenylacetylene (1) with Organometallic Gold(III) Compounds

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>cat. loading (mol %)</th>
<th>time</th>
<th>conversion [%]</th>
<th>isolated yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BzPPh₃[Au(mes)Cl₂] (3)</td>
<td>1</td>
<td>1 h 30 min</td>
<td>3&lt;sup&gt;°&lt;/sup&gt;</td>
<td>81&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>BzPPh₃[Au(mes)ClCl] (3)</td>
<td>2</td>
<td>1 h 30 min</td>
<td>100</td>
<td>81&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>BzPPh₃[Au(mes)Cl₂] (4)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>2&lt;sup&gt;°&lt;/sup&gt;</td>
<td>98&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>BzPPh₃[Au(mes)ClCl] (7)</td>
<td>2</td>
<td>1 h 30 min</td>
<td>72&lt;sup&gt;°&lt;/sup&gt;</td>
<td>70&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>[“Au(mes)₂Cl”] (8)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>100</td>
<td>98&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>[Au(mes)₂Cl(tht)]</td>
<td>2</td>
<td>1 h 30 min</td>
<td>0&lt;sup&gt;°&lt;/sup&gt;</td>
<td>0&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>cis-PPN[Au(mes)ClCl] (5)</td>
<td>2</td>
<td>1 h 30 min</td>
<td>11&lt;sup&gt;°&lt;/sup&gt;</td>
<td>11&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>cis-[Au(mes)Cl₂] (6)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>33&lt;sup&gt;°&lt;/sup&gt;</td>
<td>33&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>trans-NBu₄[Au(mes)Cl₂] (9a)</td>
<td>1.6</td>
<td>1 h 30 min</td>
<td>100</td>
<td>98&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>[“Au(mes)₂Cl”] (10)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>100</td>
<td>98&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>trans-NBu₄[Au(C₆F₅)Cl₂] (9b)</td>
<td>1.6</td>
<td>3 h 30 min</td>
<td>94&lt;sup&gt;°&lt;/sup&gt;</td>
<td>83&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>trans-NBu₄[Au(C₆F₅)Br₂] (9b)</td>
<td>2.5</td>
<td>4 h</td>
<td>96</td>
<td>90&lt;sup&gt;°&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conversion to phenyl methyl ketone (2) determined by GCMS. <sup>b</sup> Isolated compound (see Experimental Section) characterized by 1H NMR. <sup>c</sup> Starting material was recovered.

Table 2. Hydration of Phenylacetylene (1) with Au(III) or Au(I) Compounds in the Presence of Acid (1:10 Molar Ratio) or Silver Salts (1:1 Molar Ratio)

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>acid or silver salt</th>
<th>cat. loading (mol %)</th>
<th>time</th>
<th>conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BzPPh₃[Au(mes)Cl] (3)</td>
<td>HSO₃CF₃</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>23&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>BzPPh₃[Au(mes)ClCl] (7)</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>17&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>BzPPh₃[Au(mes)Cl₂] (7)</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>45&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>t-NBu₄[Au(mes)Cl₂] (9a)</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>100&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>t-NBu₄[Au(mes)Cl₂] (9a)</td>
<td>AgOSO₂CF₃</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>75&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>BzPPh₃[Au(mes)Cl] (3)</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>[Au(Me)PPh₃] (11)</td>
<td>H₂SO₄</td>
<td>1</td>
<td>1 h 30 min</td>
<td>100&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>[Au(Me)PPh₃] (11)</td>
<td>AgOSO₂CF₃</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>100&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>[Au(Me)PPh₃] (11)</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>[Au(Me)PPh₃] (11)</td>
<td>AgOSO₂CF₃</td>
<td>0.5</td>
<td>1 h 30 min</td>
<td>100&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>[Au(C₆F₅)Br₃]</td>
<td>H₂SO₄</td>
<td>0.1</td>
<td>1 h 30 min</td>
<td>15&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>[Au(C₆F₅)Br₃]</td>
<td>AgOSO₂CF₃</td>
<td>1</td>
<td>1 h 30 min</td>
<td>16&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conversion to phenyl methyl ketone (2) determined by GCMS. <sup>b</sup> Starting material was recovered.

The compound [Au(C₆F₅)Cl₂(tht)].<sup>35</sup> that can be obtained as a solid, does not catalyze the hydration of 1 (Table 1, entry 6). This is similar to what we observed (no conversion at all) with the inorganic compound [AuCl(tht)].<sup>36</sup>

Anionic and neutral organoamalgam compounds with two mesityl or pentafluorophenyl groups such as Q[AuR₂Cl₂] or [AuR₂Cl₂] were also studied. We have recently described the compound cis-PPN[Au( mes)₂Cl₂] (5),<sup>37b</sup> and it is obtained via organomercurial transmetallation. Here, we present an alternative synthesis of 5 via a less toxic way. The reaction involves a transmetallation from a mesityl gold(I) compound to PPN[AuCl₄]. In a way similar to the transmetallation of [Au(η⁵-C₅H₅)PPh₃] (NCN = [2,6-(CH₂-NMe₂)₂-C₆H₃]) to Au(III), Ni(II), Pd(II), Pt(II), Ti(IV), and Fe(III) metallic centers that has been recently reported by one of us.<sup>37</sup> We obtain pure Pt(II), Ti(IV), and Fe(III) metallic centers that has been recently described by one of us.<sup>37</sup>

However, 5 and its neutral derivative [Au(mes)₂Cl] (6) (whose dimeric structure has been confirmed by X-ray analysis)<sup>37b</sup> do not catalyze the hydration of 1 or achieve poor conversions, even in quantities of 3 mol % or after 4 h (Table 1, entries 7 and 8). Similarly, cationic or neutral derivatives of 5 (previously described)<sup>38b</sup> such as cis-[Au( mes)₃P(tol)₁Cl]Cl₂, cis-[Au( mes)₂-AsPPh₃]Cl, or cis-[Au( mes)₂(bipy)]Cl₄ do not catalyze the hydration reaction of 1 at all. Nevertheless, anionic compounds with two pentafluorophenyl groups such as trans-NBu₄[Au(C₆F₅)Cl₂] (X = Cl (9a) or Br (9b))<sup>31b</sup> are able to give the ketone product 2 in high yields. In the case of 9a, the total conversion is achieved with 1.6 mol % of catalyst. The influence of the different catalytic activity observed for compounds trans-NBu₄[Au(C₆F₅)Cl₂] (X = Cl (9a), Br (9b), I (9c))<sup>31b</sup> can be related to the electronegativity for the different halides as well as the strength of Au–X bonds. The hydration reaction of 1 does not take place when X = I (9c) under standard reaction conditions.

Neutral Au(C₆F₅)Cl₂ (10)<sup>38</sup> is prepared from 9a, and that can be isolated as a solid (Scheme 4). In situ generated 10 can be used successfully for catalytic purposes (catalyst loading 4.5 mol %, entry 10).

Scheme 2

\[
\text{BzPPh₃[AuRCI₃] + AgClO₄ or AgOTf} \quad \text{Et₂O} \\
\text{R = mes (3), C₆F₅(7)} \quad \text{R = mes (4), C₆F₅(8)}
\]

\[\text{i) } \begin{array}{c}
\text{AgCl} (\text{CH₃Cl})_n \\
\text{ii) } \text{BzPPh₃ClO₄ or BzPPh₃TfO}
\end{array}\]

Scheme 3

\[
\text{PPN[AuCl₄] + 2[Au( mes)₃PPh₃] } \quad \text{cis-PPN[Au( mes)₂Cl₃]} (5) \\
\text{-2[Au(Ph₃)₃]} \quad \text{Yield: 92%}
\]


(39) [Au(C₆F₅)Cl₂] is obtained by reaction of trans-NBu₄[Au(C₆F₅)Cl₂] and 1 equiv of AgClO₄ or AgOTf.
We performed the hydration reaction with selected organometallic gold(III) compounds 3, 7, and 9a in conjunction with acids. The addition of \( \text{H}_2\text{SO}_4 \) (in a molar ratio of 1:10, gold: \( \text{H}_2\text{SO}_4 \)) does not affect the hydration reaction in the case of \( \text{BzPPh}_3\text{Au}(\text{mes})\text{Cl}_2 \) (3) or not much in the case of \( \text{BzPPh}_3\text{Au}(\text{mes})\text{Cl}_2 \) (7) (Table 2, entries 1 and 2), but it helps the amount of catalyst to be decreased to 0.5 mol % to give total conversion in the case of \( \text{trans-NBu}_4\text{Au}(\text{C}_6\text{F}_5\text{Cl})_3 \) (9a) (entry 3). The addition of \( \text{HClO}_4 \) seems to improve a little the catalytic activity of 3 and 7 (entries 4 and 5). Again, the behavior of organometallic complexes containing mesityl or pentafluorophenyl ligands is different, pointing out perhaps the different reaction pathways.

1.2. Hydration with Gold(I) Complexes. The high catalytic activity displayed by the system \([\text{Au}(\text{Me})\text{L}]^{-}\text{acid}\) (in a 1:10 molar ratio, \( \text{L} = \text{phosphine}, \text{phosphite}, \text{or arson ligand} \)) or \([\text{AuCl}(\text{PPh}_3])^{-}\text{silver salt}\), when water and MeOH were added to alkynes, has been described by Teles\textsuperscript{29} and Tanaka\textsuperscript{30}.

We studied the catalytic activity of inorganic and organometallic gold(I) compounds in neutral media (and under standard reaction conditions) for the hydration of phenylacetylene 1. The complexes tested were anionic organometallic compounds with one or two organic radicals (such as \( \text{PPN}[\text{Au}(\text{mes})\text{Cl}]_{\text{3}} \) or \( \text{NBu}_4\text{Au}(\text{C}_6\text{F}_5\text{Cl})_2 \)) or neutral inorganic and organometallic complexes with the triphenylphosphine ligand (such as \( \text{AuCl}^{-}\text{PPh}_3 \)). Under the standard reaction conditions (2 mol % of catalyst, 1.5 h in refluxing MeOH), these compounds either do not catalyze the hydration at all or do so very poorly (20% of conversion for \([\text{AuCl}(\text{PPh}_3)]^{-}\)). This also gives evidence for the hypothesis that gold(III) compounds in neutral media do not catalyze the reactions because they decompose to gold(I) complexes. Compounds that could form supposedly catalytically active \([\text{AuPPh}_3]^+\) species easily under the reaction conditions such as \( \text{O}[\text{Au}(\text{PPh}_3)]^{-}\text{(BF}_3 \text{)} \text{ClO}_4 \) or \([\text{AuR}(\text{PPh}_3)]^{-}\text{R} = \text{C}_6\text{F}_5, \text{mes, Me}^7 \) were also studied.\textsuperscript{48} However, only with \( \text{O}[\text{Au}(\text{PPh}_3)]^{-}\text{(BF}_3 \text{)} \text{ClO}_4 \) was a conversion of 55% obtained. That perhaps may imply that the acidic cocatalyst is not only necessary to form \([\text{AuPPh}_3]^+\) fragments but it also could help to prevent the reduction from \( \text{Au(I)} \) to \( \text{Au(0)} \) and the decomposition of the catalyst.

The influence of acids as cocatalysts in the hydration of 1 was studied (Table 2). We found that, for \([\text{AuMe}(\text{PPh}_3)]^{-}\) (11) and acid (\( \text{H}_2\text{SO}_4 \) or \( \text{HClO}_4 \)) in a 1:10 molar ratio, at least 0.5 mol % of the gold compound (5 mol % of acid with respect to the alkylene) was necessary for the hydration of phenylacetylene 1 to take place (Table 2, entries 7–12).

To test the catalytic activity of \([\text{AuPPh}_3]^+\) species in neutral media (that were formed according to Teles et al. by addition of acids such as \( \text{HClO}_4 \text{CH}_3 \), \( \text{H}_2\text{SO}_4 \), or \( \text{HBF}_3 \) to \([\text{AuMe}(\text{PPh}_3)]^{-}\)) (11),\textsuperscript{29} we prepared them in situ by reaction of 1 mol % of \([\text{AuCl}(\text{PPh}_3)]^{-}\) and \( \text{AgOSO}_2\text{CF}_3 \) in a 1:11 molar ratio. However, the conversion of 1 to 2 was only 16% (entry 12). This could also support the hypothesis that the acid helps the hydration reaction not only due to the protonation of the \([\text{AuMeL}]^+\) species, but also to stabilize it.
Scheme 5

\[
\text{C} = \text{CH} \quad \xrightarrow{\Delta, \text{cat}} \quad \text{OMe} \quad \text{C} = \text{CH}_2 + \text{OMe} \quad \text{C} = \text{CH}_2
\]

(1) \quad (2) \quad (3)

Table 3. Addition of Anhydrous Methanol to Phenylacetylene (1) with Organometallic Gold(III) Compounds

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>cat. loading (mol %)</th>
<th>time</th>
<th>conversion (%)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BzPPh₃[Au(mes)Cl] (3)</td>
<td>3</td>
<td>1 h 30 min</td>
<td>26 (12)</td>
<td>64 (13)</td>
</tr>
<tr>
<td>2</td>
<td>BzPPh₃[Au(C₆F₅)Cl] (4)</td>
<td>3</td>
<td>1 h 30 min</td>
<td>45 (12)</td>
<td>55 (13)</td>
</tr>
<tr>
<td>3</td>
<td>t-NBu₄[Au(C₆F₅)Cl] (9a)</td>
<td>2.5</td>
<td>1 h 30 min</td>
<td>100 (12)</td>
<td>98</td>
</tr>
</tbody>
</table>

* Conversion to products determined by GCMS. a Isolated 12 (see Experimental Section) characterized by ¹H NMR.

Scheme 6

\[
\text{C}_7\text{H}_7\text{C} = \text{CH} \quad \xrightarrow{\text{MeOH} / \text{H}_2\text{O}, \Delta, \text{cat}} \quad \text{CH}_3\text{C}(\text{CH}_3)\text{C} = \text{CH}_3
\]

(15) \quad (16)

2. Addition of MeOH to Phenylacetylene. The addition of MeOH to phenylacetylene (1) gave two compounds with the catalytic system [AuMe(PPh₃)₃]:HSO₃CH₃ (molar ratio 1:10). The enol ether (13) and the acetal (12) are shown in Scheme 5 were obtained in a ratio of 1:2, respectively.

We tested the most representative organometallic gold(III) catalysts that had been efficient catalysts for the hydration of 1, 3, 7, and 9a. The results are collected in Table 3. To achieve a total conversion of 1 to the addition products, the catalyst loading had to be of 3 mol % in the case of anionic complexes with one organic radical (BzPPh₃[AuRCl₃]), R = mes (3), C₆F₅ (7) and 2.5 mol % in the case of trans-NBu₄[Au(C₆F₅)Cl₂] (9a). The enol ether 13 was obtained as the major product for 3, whereas it was almost obtained in a 1:1 ratio for 7 (Table 3, entries 1 and 2). However, the selectivity improved when we used 9a as catalyst, and the acetal 12 was obtained as the only product of the addition reaction (entry 3). In the case of Na[AuC₆F₅Cl], only 12 was obtained. We know that under workup conditions, 13 is converted into the ketone 2, and thus a mixture of 12 and 2 is identified by ¹H NMR.

3. Hydration and Addition of MeOH to n-Heptyne. The catalytic activity of these organometallic gold(III) compounds with a terminal aliphatic-chain alkyl was tested. The alkyl of choice was n-heptyne (15), and its hydration product (Scheme 6) 2-heptanone (16). In Table 4, we collect the hydration results for anionic organometallic gold(III) compounds such as 3, 7, and 9a or neutral compounds such as 4, 8, and 10. The results are almost identical to those obtained for the hydration of phenylacetylene (1) with the exception of compound BzPPh₃[Au(mes)Cl] (3) that catalyzes the hydration of n-heptyne (15), entry 1, but does so more poorly than it catalyzes the hydration of alkyl 1 (2 mol %), Table 1 (entry 2). Complexes with either one or two pentafluorophenyl groups (anionic or neutral) are able to give the hydration of 15 to 16 under the standard reaction conditions (Table 4, entries 3–6).

Again, the addition of acids such as H₂SO₄ or HSO₃CF₃ (10 mol % with respect to the alkyn) improves the hydration reaction, and the amounts of catalysts can be decreased to 1 mol % in the case of compounds 7 and 9a. The addition of dry MeOH to n-heptyne (15) to give the diacetal (17) or the enol ether product (18), Scheme 7, was tested. The results (Table 5) are quite similar to those obtained in the addition of MeOH to phenylacetylene (1, Table 3). Complexes BzPPh₃[AuRCl₃] afforded a mixture of acetal and enol ether 18, the latter being the major product of the reaction (entries 1 and 2). However, if we increase the amount of catalyst to 5 mol % and the reaction time from 1.5 to 3 h, the amount of the diacetal (17) can be increased (entry 3). As in the case of phenylacetylene (1), the compound with two pentafluorophenyl groups t-NBu₄[Au(C₆F₅)Cl₂] (9a) gives total conversion to the diacetal 17 in 1.5 h (2.5 mol %).

Table 4. Hydration of n-Heptyne (15) with Organometallic Gold(III) Compounds

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>cat. loading (mol %)</th>
<th>time</th>
<th>conversion (%)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BzPPh₃[Au(mes)Cl] (3)</td>
<td>2</td>
<td>1 h 30 min</td>
<td>8</td>
<td>24 (17)</td>
</tr>
<tr>
<td>2</td>
<td>[Au(mes)Cl] (4)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>0</td>
<td>72 (18)</td>
</tr>
<tr>
<td>3</td>
<td>BzPPh₃[Au(C₆F₅)Cl] (7)</td>
<td>2</td>
<td>1 h 30 min</td>
<td>100 (87)</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>[Au(C₆F₅)Cl] (8)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>t-NBu₄[Au(C₆F₅)Cl] (9a)</td>
<td>2</td>
<td>1 h 30 min</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>[Au(C₆F₅)Cl] (10)</td>
<td>4.5</td>
<td>1 h 30 min</td>
<td>100 (90)</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>BzPPh₃[Au(mes)Cl] (3)</td>
<td>1</td>
<td>1 h 30 min</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

* Conversion to 2-heptanone (16) determined by GCMS. a Isolated compound (see Experimental Section) characterized by ¹H NMR. Starting material was recovered.

Table 5. Addition of Anhydrous Methanol to n-Heptyne (15) with Organometallic Gold(III) Compounds

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>cat. loading (mol %)</th>
<th>time</th>
<th>conversion (%)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BzPPh₃[Au(mes)Cl] (3)</td>
<td>3</td>
<td>1 h 30 min</td>
<td>24 (17)</td>
<td>72 (18)</td>
</tr>
<tr>
<td>2</td>
<td>BzPPh₃[Au(C₆F₅)Cl] (7)</td>
<td>3</td>
<td>1 h 30 min</td>
<td>27 (17)</td>
<td>73 (18)</td>
</tr>
<tr>
<td>3</td>
<td>BzPPh₃[Au(C₆F₅)Cl] (7)</td>
<td>5</td>
<td>3 h</td>
<td>50 (17)</td>
<td>50 (18)</td>
</tr>
<tr>
<td>4</td>
<td>t-NBu₄[Au(C₆F₅)Cl] (9a)</td>
<td>2.5</td>
<td>1 h 30 min</td>
<td>100 (17)</td>
<td>95</td>
</tr>
</tbody>
</table>

* Conversion to products determined by GCMS. a Isolated 17 (see Experimental Section) characterized by ¹H NMR.

4. Stoichiometric Reactions between Neutral Organometallic Complexes and Phenylacetylene. One of the goals
of the present study was to identify possible metallic intermediates in the addition of water and methanol to alkynes. As was stated in the Introduction, the incorporation of organic ligands into the metallic gold(III) centers may help to stabilize and to identify (by spectroscopic methods such as NMR) possible intermediates. We already knew that the hydration and MeOH addition reaction conditions were difficult to reproduce with NMR techniques as it involved the use of refluxing methanol. We were also aware that, most probably, the first step in the reaction may be the cleavage of an Au(III)—Cl bond (and elimination of QC1) and that this step required an activation energy; the conversion of 1 with t-NBu4[Au(C6F5)2Cl]3 at room temperature is very low (30% after 11 days, and it remains the same after 24 days), whereas 1 can be hydrated totally with the compound [Au(C6F5)2Cl]2; at room temperature after 11 days. That is why neutral compounds such as [Au(C6F5)Cl2]2 (8) and [Au(C6F5)2Cl]2 (10) reacted with phenylacetylene (1) in a stoichiometric way. Complexes 8 and 10 can be obtained from the anionic 7 or 9a by reaction with silver salts (Schemes 2 and 4). We assumed that the reaction of these neutral compounds (that have been able to give the addition of water and MeOH to terminal alkynes) with 1 could enable us to identify some gold(III)-alkyne intermediates.

To the best of our knowledge, although some gold(I)-alkyne complexes have been detected and isolated at low temperature, the reactions of alkenes and alkynes with gold(III) halides are often complex and lead to at least partial reduction of gold(III) to gold(I) in most cases (even at low temperatures). There are not any gold(III)-alkyne products known to date, although some gold(III)-vinyl intermediates have been isolated in reactions of alkyl-gold(I) compounds with alkynes or AuCl3 with dimethylacetylene.

The addition of PhCCH (in a molar ratio of 1:1) to [Au(C6F5)-Cl]2 2 (8), prepared in situ in Et2O as detailed in Scheme 2 and the Experimental Section, at room temperature results in a rapid change of color of the solution from colorless to bright yellow, orange, and then subsequent decomposition to metallic gold in a few seconds. However, the reaction can be carried out at −80 °C, and in a few minutes the solution of 8 becomes yellow by addition of 1. When we tried to isolate the possible metallic products (by removal of solvent), abundant metallic gold is produced within a few seconds. The obtained residue is dissolved in C6D6 and analyzed by 1H and 19F{1H} NMR at room temperature. The obtained spectra are very complicated, and we can only deduce that phenylacetylene (1) has reacted completely and that there are mixtures of gold(III) complexes containing C6F5 groups, C6F5-containing organic products, and phenyl methyl ketone (2).

4.1. Reaction of [Au(C6F5)2Cl]2 with Phenylacetylene. Compound [Au(C6F5)2Cl]2 (10) can be obtained as a solid (Scheme 4, Experimental Section), although with a small impurity of NBu4 ClO4. Compound 10 is very unstable in solution (especially in chlorinated solvents such as CH2Cl2 or CHCl3), and it decomposes to gold(I) compounds and metallic gold after a few minutes at room temperature. Compound 10 is insoluble in less polar solvents such as toluene or benzene and soluble in Et2O, THF, and MeOH. We carried out the reaction between 10 and 1 at low temperature. The solvent of choice was toluene for 10, which was insoluble. However, the addition of 1 at −80 °C gives a partial solution of 10 and a change of color of the resulting solution (colorless to orange). When trying to remove solvents (above −50 °C) to isolate gold compounds, we observed a very fast darkening of the solution and decomposition to metallic gold. We followed the reaction by NMR techniques (1H and 19F{1H}), and thus we carried out the stoichiometric reaction of 10 and 1 in dry toluene-d8 at −80 °C. At this temperature, we mostly observed in the 1H NMR spectrum the signals of the solvent and unreacted phenylacetylene (1). When the temperature is increased to −60 °C, some new signals (apart from those corresponding to unreacted phenylacetylene at 2.42 (s, PhCC)), 6.90 (m), and 7.25 ppm (d (PhCCH)) can be observed in the 1H NMR spectrum. The signals appear at 3.23 (s), 5.80 (s), and 7.9 (s, br) ppm and have approximately the same intensity. A broad signal (with less intensity) appears at 3.76 (s) ppm. The19 F NMR at −60 °C spectrum (Figure 1) is complicated and shows different signals that can be assigned to F (in ortho, para, and meta positions) from the C6F5 radicals. In general, for C6F5 groups, the signals in the ortho and meta positions can appear to be very complicated (second-order spectra) due to the couplings between F in ortho and meta positions. From the chemical shifts of the signals assigned to F in the ortho position, we can propose that they belong to the gold(III) species (as they appear between −120 and −124 ppm). The number of signals in the F para zone is more indicative of how many different C6F5 groups we have (or else of how many different C6F5-containing compounds we may have).

In this case, we observe the existence of five signals with appreciable intensity. The signals could be assigned to two different gold(III) compounds with the two C6F5 groups in a cis configuration (and thus with different substituents). The fifth signal could be assigned to a gold(III) species with the two C6F5 groups in a trans configuration. The signals appear as broad triplets at −154.4 and −156.2 ppm (for a gold(III) compound with two cis-C6F5 groups, species A, Figure 2), at −156.8 and −157.1 ppm (for the other gold(III) complex with two C6F5...
groups in a cis disposition, species B, Figure 2) and at $-157.9$ ppm (for the compound with two $C_6F_5$ groups in a trans disposition, species C, Figure 2). The chemical shifts of the F in ortho positions are consistent with gold(III) compounds and not with gold(I) species.

The $^1H$ and $^{19}F$-$^1H$ NMR spectra at $-50$ °C are almost identical. At this temperature, a $^{19}F$-$^1H$ COSY NMR experiment was carried out. From this spectrum, we can make the assignment of related F in ortho positions with identical intensity, whereas the signal at 3.85 (s) ppm (3.76 ppm at 0 °C) has almost disappeared. Signals corresponding to the NBu₄ClO₄ appear with almost the same intensity, whereas the signal at 5.28, 5.37, 6.09, 6.27, 6.03, 6.47, and 6.57 ppm (as singlets). At this temperature, the $^{19}F$-$^1H$ NMR is quite similar to that recorded at $-20$ °C, although new signals (whose F in ortho positions that appear at around $-140$ ppm can be assigned to organic $C_6F_5$-containing products) are observed.

The $^1H$ NMR spectra recorded between $-80$ and $0$ °C allowed us to propose that the signals observed at 3.66 and 5.99 ppm (and that remain from $-80$ to $0$ °C) may correspond to the proton from phenylacetylene (I) that has reacted with [Au-(C₆F₅)₂Cl]₂ (10). The signal that appears at 3.76 (at $-80$ °C) should also correspond to a proton from I that has reacted with 10. We think that this signal may possibly correspond to a signal of a terminal proton of a phenylacetylene moiety (I) coordinated to a metallic center (in this case, gold(III)) as a two-electron ligand (Figure 4).

The two signals that appear at 3.23 and 5.80 ppm (at $-80$ °C) or at 3.66 and 5.99 ppm (at 0 °C) with identical intensity should correspond to those of a terminal proton and a hydroxyl group from a coordinated phenylacetylene to a gold(III) center such as a vinyl ligand (Figure 5), most plausibly generated by nucleophilic attack of an OH⁻ to the gold(III)-alkyne intermediate shown in Figure 4.

The signal of the OH proton should be at 3.76 ppm, whereas the signal of the terminal proton (coming from the phenylacetylene moiety and in a cis disposition with respect to the OH group) may be at 3.23 ppm. Similar chemical shifts have been found in π-vinyl alcohol complexes of Os(II) formed by quantitative reaction of the alkynyl complex [Os(NH₃)(η²-CH₂CCCH₂)]²⁺ with water. Moreover, this complex seems to be a plausible intermediate as it has been reported that the reaction of Au₂Cl₆ with dimethylacetylene (DMA) and pyridine affords a gold(III)-vinyl complex that can be spectroscopically characterized by $^1H$ NMR at $-40$ °C (CH₂Cl₂). The proposed structure of this vinyl intermediate is shown in Figure 6. Besides, the gold(III) compounds cis-[trans-AuMe₂(C₆F₅)]$^-$ and cis-[cis-AuMe₂(C₆F₅)]$^-$ could

![Figure 2](image-url). Different gold(III) species identified as major products in the $^{19}F$-$^1H$ NMR spectrum of the reaction of I and 10 in toluene-$d_8$ at $-60$ °C (square, triangle, and circle represent different substituents).

![Figure 3](image-url). $^1H$ NMR spectrum of the reaction of I and 10 in toluene-$d_8$ at 0 °C.

![Figure 4](image-url). Plausible gold(III)-alkyne intermediate ($^1H$ NMR signal of terminal H at 3.76 ppm).

![Figure 5](image-url). Plausible gold(III)-vinyl intermediate.

![Figure 6](image-url). Proposed gold(III)-vinyl intermediate in the reaction of Au₂Cl₆ with DMA and pyridine.

be isolated (although they were not properly characterized) by reaction of cis-[{Me}_{3}P]Au[(F_{2}C)C\equiv(C(F)\equiv(CF)\equiv(CF)}_{2}\text{trans-AuMe}_{2}(PMe)_{3}] or cis-[{Me}_{3}P]Au[(F_{2}C)C\equiv(C(F)\equiv(CF)\equiv(CF)}_{2}\text{cis-AuMe}_{2}(PMe)_{3}] with HCl, respectively.

Although it is quite difficult to connect the H signals (observed in the proton NMR spectra) to the signals assigned to pentafluorophenyl groups (observed in the $^{19}$F NMR spectra), we may make the following assumption. At low temperature (from $-80$ to $0^\circ C$), we mainly observed signals that can be assigned to pentafluorophenyl groups of two different gold(III) species that are in a cis disposition. We believe that these compounds (shown in Figure 2, species A and B) are also those represented in Figures 4 and 5 (whose terminal protons are detected by $^{1}H$ NMR at low temperature ($-80^\circ C$)).

At $20^\circ C$, we observe in the $^{19}$F-$^{1}H$ NMR spectrum how the signals corresponding to PhCOCH$_3$ (56) Long, D. A.; Seele, D. Spectrochim. Acta 1996, 118, 10469.

At $90^\circ C$, the $^{1}H$ NMR and $^{19}$F-$^{1}H$ NMR spectra are almost identical. The nature of the final products can be confirmed by a GC-MS analysis of the sample (after removal of the toluene-deuterated phenylacetylene), addition of MeOH, and filtration of abundant metallic gold through silica. We can identify complexes 2 (retention time 6.69 min), C$_6$F$_5$-C$_6$F$_5$ (19, 7.29 min), cis- and trans-stylylene (10.10 and 11.50 min), and cis-pentafluorophenylphenylethylene (20, 13.01 min). Although the molecular peak of 20 does not appear in its mass spectrum, peaks that can be assigned to species such as [C$_7$H$_9$] (m/z = 91), [C$_6$F$_5$ + C] (m/z = 179), and [M − Ph] (m/z = 194) can be identified.

To gain more information about the nature of the plausible gold(III) intermediates, we carried out the stoichiometric reaction of compound 10 and deuterated phenylacetylene (21) at the NMR scale (molar ratio 1:1). The reaction was followed by $^{1}H$-$^{19}$F NMR in nondeuterated toluene at different temperatures. However, in our hands, we did not get satisfactory data. To obtain a proper deuterium spectrum, long acquisition times (minimum of 0.5 h) are necessary, and, even at low temperatures, the reaction evolves quite quickly.

4.2. Proposed Mechanism for the Hydration of Phenylacetyle in with [Au(C$_6$F$_5$)$_2$Cl]. Although we have not been able to isolate gold(III) intermediates for the addition of water and MeOH to terminal alkenes, we believe that we have identified spectroscopically at low temperature the gold(III)-alkyne and the gold(III)-vinyl intermediates for these reactions. We have confirmed that organometallic gold(III) compounds with pentafluorophenyl as ligand do not decompose to gold(I) intermediates in their reaction with phenylacetylene. Gold(III) C$_6$F$_5$-containing species (cis and trans) could be identified at low temperatures, whereas at higher temperatures decomposition to metallic gold and organic C$_6$F$_5$-containing products did occur.

The presence of final product 20 (although in small amounts) confirms that the alkyne has been coordinated to the organometallic gold(III) center at some point. The obtention of phenyl methyl ketone (2) as the hydration product also leads to the hypothesis of a gold(III)-alkyne intermediate that may suffer a

C$_6$F$_5$-C$_6$F$_5$ (19). 56 We also observe signals at $-139.3$ (d, F$_0$), $-154.3$ (t, F$_p$), and $-162.6$ (q, Fm). We propose that this compound is that showed in Figure 8 (20). In the $^{1}H$ NMR spectrum at $80^\circ C$, the signals of the vinyl protons (the phenyl protons cannot be observed as they are overlapped by other signals) appear as a complicated signal at 5.91 that can be described as a triplet of triplets of doublets. The coupling between the two protons must be very small, and thus the signal appears as a ttd ($^{3}J_{F_0-H} = 10$ Hz, $^{3}J_{F_m-H} = 7$ Hz, $^{3}J_{H-H} = 3$ Hz). Signals corresponding to cis- and trans-stylylene can also be observed (although phenyl protons are overlapped by other major products).

At 90°C, the $^{1}H$ NMR and $^{19}$F-$^{1}H$ NMR spectra are almost identical. The nature of the final products can be confirmed by a GC-MS analysis of the sample (after removal of the toluene-deuterated phenylacetylene), addition of MeOH, and filtration of abundant metallic gold through silica. We can identify complexes 2 (retention time 6.69 min), C$_6$F$_5$-C$_6$F$_5$ (19, 7.29 min), cis- and trans-stylylene (10.10 and 11.50 min), and cis-pentafluorophenylphenylethylene (20, 13.01 min). Although the molecular peak of 20 does not appear in its mass spectrum, peaks that can be assigned to species such as [C$_7$H$_9$] (m/z = 91), [C$_6$F$_5$ + C] (m/z = 179), and [M − Ph] (m/z = 194) can be identified.

To gain more information about the nature of the plausible gold(III) intermediates, we carried out the stoichiometric reaction of compound 10 and deuterated phenylacetylene (21) at the NMR scale (molar ratio 1:1). The reaction was followed by $^{1}H$-$^{19}$F NMR in nondeuterated toluene at different temperatures. However, in our hands, we did not get satisfactory data. To obtain a proper deuterium spectrum, long acquisition times (minimum of 0.5 h) are necessary, and, even at low temperatures, the reaction evolves quite quickly.

4.2. Proposed Mechanism for the Hydration of Phenylacetyle in with [Au(C$_6$F$_5$)$_2$Cl]. Although we have not been able to isolate gold(III) intermediates for the addition of water and MeOH to terminal alkenes, we believe that we have identified spectroscopically at low temperature the gold(III)-alkyne and the gold(III)-vinyl intermediates for these reactions. We have confirmed that organometallic gold(III) compounds with pentafluorophenyl as ligand do not decompose to gold(I) intermediates in their reaction with phenylacetylene. Gold(III) C$_6$F$_5$-containing species (cis and trans) could be identified at low temperatures, whereas at higher temperatures decomposition to metallic gold and organic C$_6$F$_5$-containing products did occur.

The presence of final product 20 (although in small amounts) confirms that the alkyne has been coordinated to the organometallic gold(III) center at some point. The obtention of phenyl methyl ketone (2) as the hydration product also leads to the hypothesis of a gold(III)-alkyne intermediate that may suffer a
nucleophilic attack of a OH\textsuperscript{-} molecule. With all of the collected spectroscopic and chromatographic data, we would like to propose the following mechanism for the hydration of phenylacetylene (1) with [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Cl]\textsubscript{2} (10) as catalyst (Scheme 8).

First, the alkyne coordinates to the organometallic gold(III) complex as a two-electron ligand to give \textsubscript{22}. The water molecule (dissociated in H\textsuperscript{+} and OH\textsuperscript{-}) in polar solvents such as MeOH reacts with \textsubscript{22} to give \textsubscript{23} by nucleophilic attack of the OH\textsuperscript{-} group. The attack is produced on the carbon that contains the aryl substituent and that would generate, therefore, the more stable carbocation. The H\textsuperscript{+} can generate a stable ionic complex \textsubscript{23} as shown in Scheme 8, or it can generate HCl, giving a neutral complex with a coordinated solvent molecule. A subsequent keto–enol equilibrium would afford intermediate \textsubscript{24} that would give phenyl methyl ketone (2) and regenerate 10 as the catalyst by reaction with H\textsuperscript{+} that is present in the medium (or HCl). The presence of at least one chloride ligand coordinated to the gold(III) center seems essential for the reaction to proceed.

In the case of ionic gold(III) compounds, the first step may imply the dissociation of one chloride ligand and elimination of QCl from the gold(III) precatalyst to generate the plausible gold(III) active ["AuCl\textsubscript{3}"], ["AuCl\textsubscript{2}R"], or ["AuClR\textsubscript{2}"] catalytic species. The reactions need refluxing MeOH temperature to proceed, although in the case of neutral [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Cl]\textsubscript{2} (10) total conversion of 1 to 2 can be achieved at room temperature after 11 days. These gold(III) catalytic species decompose to gold(0), and, in the case of organometallic compounds, they give organic R–R compounds by reductive carbon–carbon coupling under reaction conditions. Examples of such gold-mediated couplings are well documented in the literature.\textsuperscript{55}

We believe that the addition of some acidic cocatalysts to these gold(III) complexes improve their catalytic activity a little because they prevent the reduction to metallic gold.

The mechanism of gold(I) complexes is different. We believe that the catalytic species are [AuL]\textsuperscript{+} stable fragments that can coordinate an alkyne molecule (as claimed by Teles and co-workers\textsuperscript{29} and Tanaka et al.\textsuperscript{30}). However, the addition of acidic cocatalysts in this case not only helps to form stable [AuL]\textsuperscript{+} fragments (generated from [AuMeL]/acid) but may also prevent the decomposition of these catalytic gold(I) systems to gold(0) species.

Conclusion

In summary, we have proven that anionic and neutral organometallic gold(III) complexes (with one or two organic radicals) are able to catalyze the addition of water and methanol to terminal alkynes with a catalytic activity similar to that reported for Na[AuCl\textsubscript{4}]. The addition reactions follow the Markovnikov rule, giving the corresponding ketones or diacetel products. The reactions take place in neutral medium, although the addition of acidic cocatalysts improves their catalytic activity (plausibly by avoiding the decomposition of these catalysts to metallic gold(0)). The presence of at least one chloride ligand coordinated to the gold(III) center seems essential for the reaction to proceed, whereas the presence of even weakly coordinating neutral ligands seems to inhibit the catalytic process. Anionic complexes need refluxing methanol temperature, whereas neutral complexes are able to catalyze the hydration of alkynes at room temperature in neutral medium (although very slowly). The pentafluorophenyl ligand coordinated to gold(III) centers behaves in a way similar to chloride ligands. It seems that gold(III) compounds are the active catalytic species for these processes as gold(I) intermediates were not identified by spectroscopic methods. Moreover, the spectroscopic study of stoichiometric reactions between the complex [Au(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Cl]\textsubscript{2} and phenylacetylene at variable temperature has allowed us to identify two plausible gold(III) intermediates for the hydration reactions. Thus, we propose that the terminal alkyne coordinates to a gold(III) center as the first step of the reaction and ulterior nucleophilic attack of an hydroxyl group to the coordinated alkyne gives a gold(III)-vinyl intermediate.
that by subsequent keto–enol equilibrium is able to form the ketone and regenerate the initial gold(III) catalytic species. We were able to prove that the decomposition of the catalyst is due to reductive elimination at the gold(III) center, giving the coupling organic product bis-pentafluorophenyl and metallic gold.

Furthermore, the present study demonstrates that organometallic gold(III) complexes behave similarly to Lewis acids. More importantly, the incorporation of organic fragments to the gold(III) centers not only seems to stabilize plausible metallic intermediates in nucleophilic additions to triple bonds but it also has helped to identify these intermediates by spectroscopic methods. A rational design and synthesis of organic and inorganic ligands able to coordinate to gold(III) and gold(I) centers that can modify electronic and steric properties and, thus, improve their catalytic activity in different chemical processes is, therefore, anticipated.

Additions of nucleophiles to triple and double bonds catalyzed by gold(III) and gold(I) organometallic and inorganic compounds are currently under investigation by our research group.

Experimental Section

General Methods. All reactions with air- or water-sensitive compounds were carried out under standard Schlenk line techniques. Reactions of gold compounds with silver salts must be carried out under argon over activated 4 Å molecular sieves. BzPPh3 ClO4, precipitated, and was removed by filtration. Solutions of [Au(mes)Cl2] (4) and [AuCF3Cl2] (8) in cold Et2O could be used subsequently. The complex cis-PNP[Au(mes)Cl2] (5) was prepared via an alternative gold(I)-transmetalation method (which prevents the use of toxic [Hg(mes)2]).

Preparation of cis-PNP[Au(mes)Cl2] (5). To a solution of PNP[AuCl] (0.438 g, 0.5 mmol) in 30 mL of acetone was added [Au(mes)(PPh3)] (0.723 g, 1.25 mmol). The reaction mixture was refluxed for 2 h. The resulting colorless solution was then cooled at room temperature and concentrated to ca. 5 mL. When 40 mL of toluene was added, the compound cis-PNP[Au(mes)Cl2] (5) was obtained as a white solid. The crude product was filtered and washed with 3 × 20 mL of toluene. After being dried under vacuum, cis-PNP[Au(mes)Cl2] (5) was obtained as a pure compound and could be used without further purification (0.485, 92% yield). The toluene filtrate was concentrated to ca. 5 mL, and when 20 mL of cold n-hexane was added, [AuCl2(PPh3)] precipitated as a white solid. The solid was obtained in 85% yield (0.841 g) as an analytically pure compound.

General Procedure for the Hydration of Terminal Alkynes. 1. Neutral Media. To a stirrill solution of 1 mmol of phenylacetylene (1) (0.110 mL) or n-heptyne (15) (0.130 mL) and water (0.5 mL) in 5 mL of MeOH was added the amount of gold compound as specified in Tables 1, 2, and 4, and the mixture was heated at reflux for 90 min for 4 h. Prior to workup, the metallic gold that formed was removed by filtration through a short silica column, and the resulting filtrate was analyzed by GCMS. If conversions were higher than 90%, the reaction mixture was concentrated under reduced pressure and the residue was diluted with Et2O and washed with 1:1 mixture of brine and aqueous ammonia. The ethereal solution was dried over anhydrous MgSO4 and concentrated to give the products (phenyl methyl ketone (2) or 2-heptanone (16)) as pure colorless oils as characterized by 1H NMR (see Supporting Information).

2. Acidic Media. To a stirrill solution of 1 mmol of phenylacetylene (1) (0.110 mL) or n-heptyne (15) (0.130 mL) and water (0.5 mL) in 5 mL of MeOH was added the amount of gold compound and acid (HtF or H2 SO4) in a molar ratio 1:10 as specified in Tables 2 and 4, and the mixture was heated at reflux for 90 min. Prior to workup, the metallic gold formed was removed by filtration through a short silica column, and the resulting filtrate was analyzed by GCMS. If conversions are 90% or higher, we followed the previously described procedure to obtain 2 or 16 as pure colorless oils.

General Procedure for the Addition of Methanol to Terminal Alkynes. To a solution of 1 mmol of phenylacetylene (1) (0.110 mL) or n-heptyne (15) (0.130 mL) in 5 mL of anhydrous MeOH was added the amount of gold compound as specified in Tables 3 and 5, and the mixture was heated at reflux under Ar for 90 min. The reaction mixture was analyzed by GCMS (after addition of 0.5 mL of triethylamine and elimination of metallic gold). If the conversion was higher than 90%, we follow the previously described workup to obtain compounds 12 and 17 as pure colorless oils or mixtures of 2/12 and 16/17 (see Tables 3 and the Results and Discussion section) as characterized by 1H NMR (see Supporting Information).

Stoichiometric Reaction between [Au(C6F5)2Cl] (10) and Phenylacetylene (1). To a solution of 0.023 g (0.04 mmol) of [Au(C6F5)2Cl]; (10) in 0.5 mL of dry toluene-d8 at −80 °C (NMR tube) was added phenylacetylene (1) (5 µL, 0.04 mmol) at this temperature, and the tube was placed immediately in the NMR probe that had been cooled to −80 °C. 1H and 19F NMR spectra were recorded at −80, −60, −50, −20, 0, 20, 40, 60, 80, and 90 °C. A 19F(H)–19F(H) COSY NMR experiment was carried out at −50 °C (before warming the reaction mixture to 0 °C, see tabulated data in Supporting Information). The final mixture was concentrated to dryness and dissolved with 2 mL of MeOH. Metallic gold was removed by filtration through a silica
column, and the resulting MeOH solution was subsequently analyzed by GC-MS chromatography. The collected NMR and chromatographic data are presented in the Discussion section, and detailed tabulated data have been collected in the Supporting Information section.

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Supporting Information Available: Tables of spectroscopic and analytical data from varying gold catalysts; spectral and chromatographical data for all organic reaction products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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