JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo401325t • Publication Date (Web): 29 Jul 2013

Aryl-Substituted Cyclopropyl Acetylenes as Sensitive Mechanistic Probes in the Gold-Catalyzed Hydration of Alkynes. Comparison to the Ag(I), Hg(II) and Fe(III)-Catalyzed Processes

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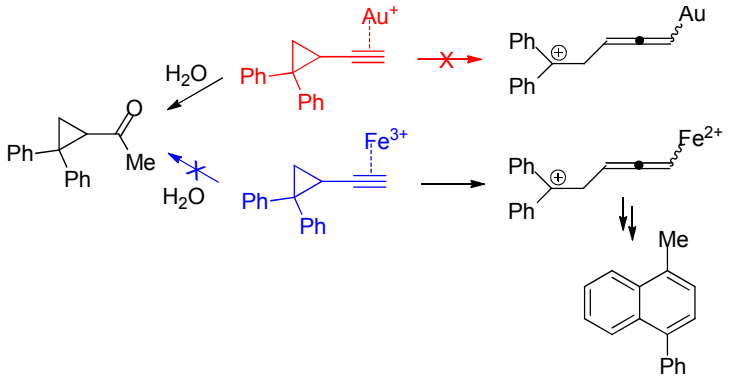
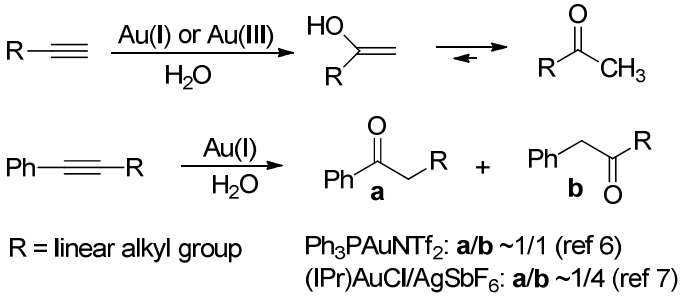


ABSTRACT: The gold-catalyzed hydration of 2-phenyl or 2,2-diphenylcyclopropyl acetylene, sensitive probes to trace the formation of vinyl carbocations, provide exclusively the corresponding cyclopropyl methyl ketones. On the other hand, in the Ag(I) or Fe(III)-catalyzed hydration, a profound vinyl carbocationic character appears in the initially formed metal-alkyne complexes, as judged by the partial (Ag^{+}) or exclusive (Fe^{3+}) formation of allene-type rearrangement products. These findings provide clear evidence for subtle electronic differences in metal-alkyne complexes including Au(I or III), Ag(I), Fe(III) and Hg(II).

Homogeneous gold(I or III) activation of alkynes is nowadays one of the most active topics in synthetic organic chemistry.[1] In the same context, the interest in the activation of alkynes by gold nanoparticles under heterogeneous conditions is constantly growing.[2] The fascinating catalytic properties of gold are attributed to a relativistic effect which stabilizes the outermost $6s^2$ electron pair, thus the reactivity and catalytic efficiency are governed by its high energy 5d orbitals.[3] Alkyne activation is promoted by coordination of Au(I) to alkynes which enhances their electrophilicity towards intra or intermolecular nucleophilic attack, providing thus a vast array of reaction pathways via unprecedented skeletal rearrangements, especially when the nucleophile is a π bond. Among the various reaction motifs in organogold chemistry studied so far, the Au-catalyzed hydration of alkynes has been proven as an extremely practical method for their transformation into carbonyl compounds (Scheme 1).[4-5] Terminal alkynes provide exclusively Markovnikov selectivity yielding methyl ketones. On the other hand, internal alkynes exhibit moderate regioselectivity. Surprisingly if one of the substituents is a phenyl group the selectivity is peculiar and depends on the catalyst. This is exemplified in the $Ph_3PAuNTf_2$-catalyzed hydration of $PhC{\equiv}CC_6H_{13}$,[6] where the two regioisomeric ketones **a** and **b** (Scheme 1) are formed in equimolar

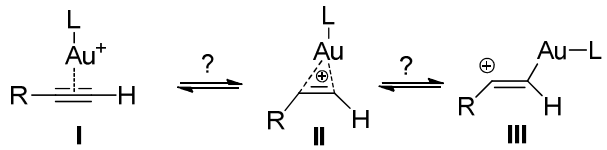


Scheme 1. The gold-catalyzed hydration of alkynes.

amounts, and in the (IPr)Au(I)-catalyzed hydration of $PhC{\equiv}CCH_2CH_3$,[7] where a formal anti-Markovnikov selectivity was observed (Scheme 1). In general, the gold-catalyzed hydration of alkynes can be achieved in the presence of Au(I),[6-12] Au(III),[13-16] Au(I) in combination with acids,[17-21] or by "type II Au(I)-Ag(I) bimetallic" systems.[22] Mechanistic studies were also reported regarding this transformation which emphasize the importance of *gem*-diaurated intermediates via a dual activation mechanism,[23] and the pivotal role of protic solvents (e.g. methanol) into the energy reaction profile.[24-25] On the basis of the lack of an apparent trend of Markovnikov selectivity in the case of phenyl-alkyl substituted internal alkynes (e.g. the examples shown in Scheme 1), the >99% Markovnikov selectivity in the gold-catalyzed hydration of terminal alkynes might be seen as rather surprizing. It is reasonable from the first point of view, that the regioselectivity is controlled by the electrophilic nature of the *sp*-carbons of the triple bond upon interaction to Au(I or III). The interaction of ionic gold to a terminal alkyne (e.g. propyne) has been computed to be slightly unsymmetrical. The bonding interaction of the metal with the internal sp-carbon atom is longer than the analogous distance to the terminal one.[16,26] This rationalizing concept provides tentative clues for the higher electrophilicity of the internal sp-C atom in the hydration process. Yet, these arguments contradict the cases of phenyl-alkyl substituted internal alkynes, where acetophenones should primarily or exclusively be anticipated.

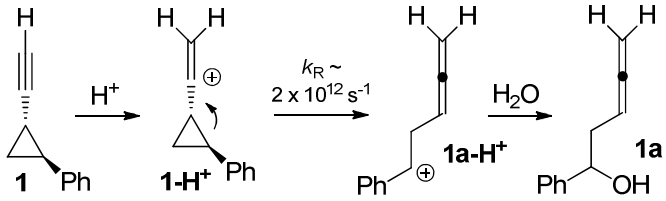
In this manuscript we explore through the gold-catalyzed hydration of terminal alkynes the nature of the ionic gold interaction to a C-C triple bond, and more specifically, whether a "loose" complex (symmetrical **I**; unsymmetrical **II**), or a formal vinyl carbocation **III** are formed (Scheme 2). The existence of vinyl gold carbocations such as **III**, could be traced by using aryl-substituted cyclopropyl alkynes as sensitive

mechanistic probes. Such substrates have been tested as probes in the past to distinguish among polar or radical pathways[27-30] in addition reactions to alkynes. For instance,



Scheme 2. Possible structures resulting from the interaction of Au^+ to a terminal alkyne (L=ligand).

trans-(2-phenyl)cyclopropan-1-yl alkyne **1** (Scheme 3) has been used by Baines and co-workers[31] to study the mechanism of its hydration catalyzed by sulphuric acid. It was found that vinyl carbocation **1-H$^+$** (from protonation of **1**) rearranges into allenyl carbocation **1a-H$^+$** at a high rate constant of approximately $k_R \sim 2x10^{12}$ s^{-1}. Subsequently **1a-H$^+$** undergoes nucleophilic attack from a H_2O molecule to yield allenyl alcohol **1a**. Alkyne **1** could therefore be considered as a quite appropriate probe to trace



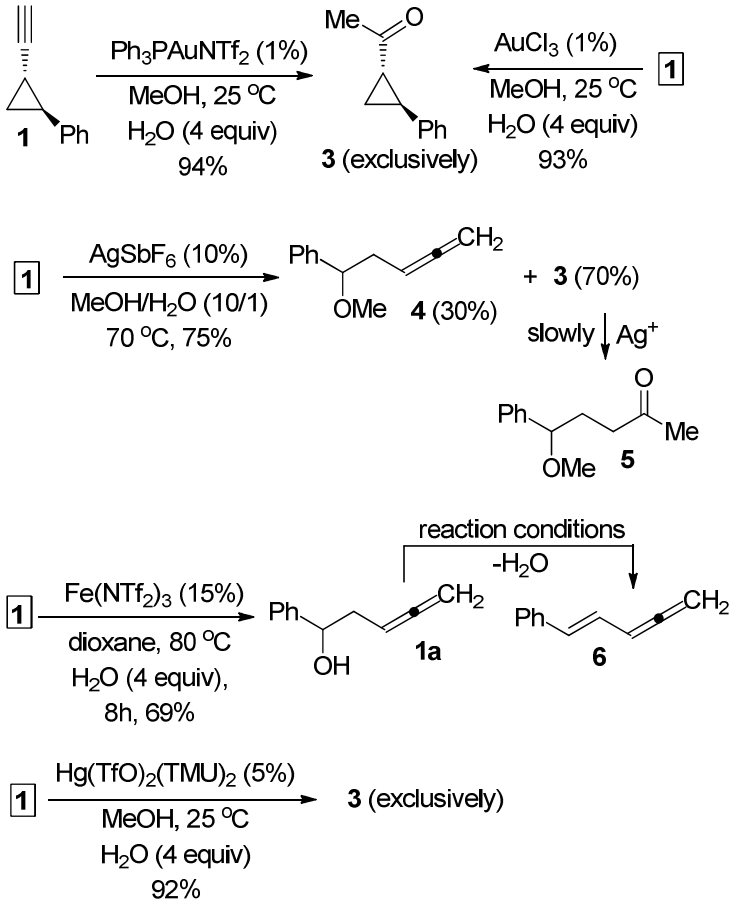
Scheme 3. The acid-catalyzed hydration of cyclopropyl alkyne **1**.[31]

the existence of vinyl carbocations during the activation of alkynes by ionic gold. Thus, we undertook the examination of the gold-catalyzed hydration of **1**, as well as, its *gem*-diphenyl analogue **2**, which is anticipated to be an even more sensitive probe. The synthesis of **1** and **2** was accomplished based on known literature protocols.[28,31] For

comparison purposes, the hydration of **1** and **2** was studied under known Ag(I),[32] Fe(III)[33] and Hg(II)[34]-catalyzed protocols and provided fruitful information regarding the nature of the intermediates under these conditions.

To study the Au-catalyzed hydration of cyclopropyl alkyne **1** we adopted the protocol by Leyva and Corma[6] using the Au(I)-based $Ph_3PAuNTf_2$ (1 mol%) as catalyst and methanol as solvent containing 4 equiv of H_2O. For the Au(III)-catalyzed hydration, $AuCl_3$ (1 mol%) in methanol containing 4 equiv of H_2O was utilized as catalyst. We wish to report herein that replacing acetonitrile as the solvent of an existing $AuCl_3$-catalyzed hydration protocol[16] with methanol, resulted to an approximately 5-10 fold enhancement of the reaction rate. It was found that under both catalytic conditions, **1** is cleanly transformed after 14 h ($Ph_3PAuNTf_2$) or ~1 h ($AuCl_3$), respectively, into methyl ketone **3** in almost quantitative yields (Scheme 4). No rearrangement products were detected. The hydration of **1** under catalysis by $AgSbF_6$[32] (10 mol%) in refluxing MeOH/H_2O=10/1 for 24 h, provides initially a mixture of **3** and the rearranged methanol-captured allene **4**[35] in a ~70/30 relative ratio and 75-80% yield. Methyl ketone **3** gradually reacts with methanol under the reaction conditions through a profound Ag^+-catalyzed activation of the carbonyl moiety, leading in part to rearranged methoxy ketone **5**[36]. This side-pathway was verified by the independent treatment of **3** with $AgSbF_6$ in MeOH. In the presence of *in situ* generated $Fe(NTf_2)_3$[33] (15 mol%) only the allene bearing rearrangement products **1a**[31] and **6**[37] were seen as an almost equimolar mixture (1,4-dioxane as solvent; 4 equiv H_2O; 80 ^oC, 8h, 69% yield), without any ketone **3** being formed. This outcome resembles the H_2SO_4-catalyzed hydration of **1** which yields **1a**.[31] The relative ratio of **1a/6** depends on reaction time, as conjugated allenene **6** is a secondary product obtained via dehydration of the initially formed allenyl alcohol **1a** under the reaction conditions. On prolonged reaction time (24 h), **1a**

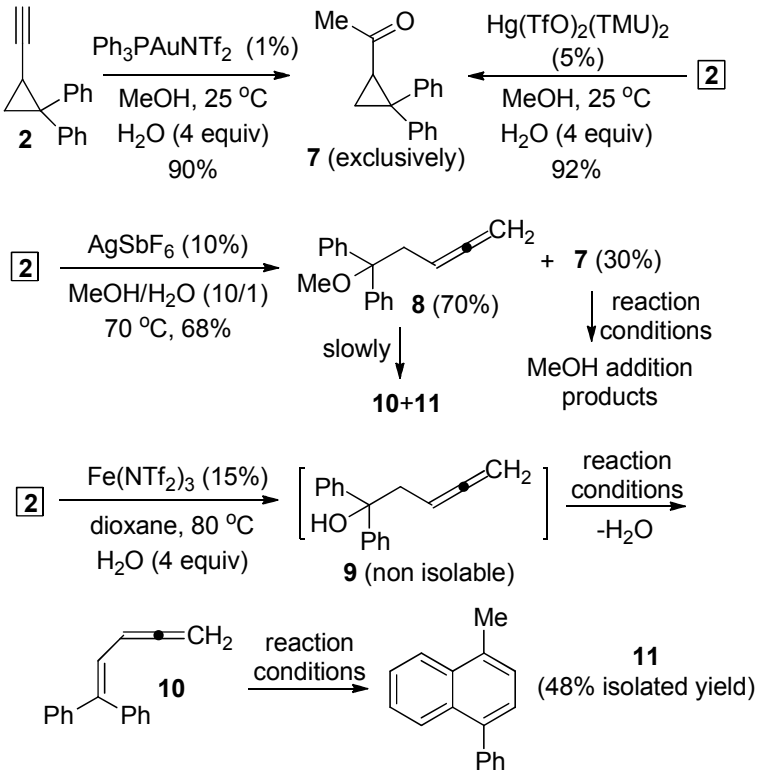
completely dehydrates into relatively labile **6**. Finally, the $Hg(TfO)_2(TMU)_2$-catalyzed[34] (TMU: 1,1,3,3-tetramethylurea) hydration of **1** in methanol (5 mol% catalyst loading, 4 equiv of H_2O), afforded exclusively ketone **3** (92% isolated yield), just as under gold catalysis conditions.



Scheme 4. The hydration of cyclopropyl-substituted alkyne **1** catalyzed by Au(I or III), Ag(I), Fe(III) and Hg(II).

We next focused on studying the hydration of *gem*-diphenyl analogue **2** under the same catalytic conditions. Alkyne **2** is foreseen as an even more sensitive mechanistic probe relative to **1**. The products from the hydration of alkyne **2** are presented in Scheme 5. Its $Ph_3PAuNTf_2$-catalyzed hydration cleanly afforded methyl

ketone **7**[38] as the only reaction product (~90% yield). Cyclopropyl methyl ketone **7** was also exclusively formed in the presence of $Hg(TfO)_2(TMU)_2$ in >90% isolated yield. On contrary, the $AgSbF_6$-catalyzed hydration results primarily to a mixture of rearranged methoxy allene **8** and ketone **7** in a relative ratio **9/7**~7/3. During the progress of the reaction, **7** gradually decomposes forming methanol adducts, while minor amounts (~10% in total) of allenene **10** and naphthalene **11** were detected after reaction completion, which probably derive via elimination of methanol from **8**. Finally, the

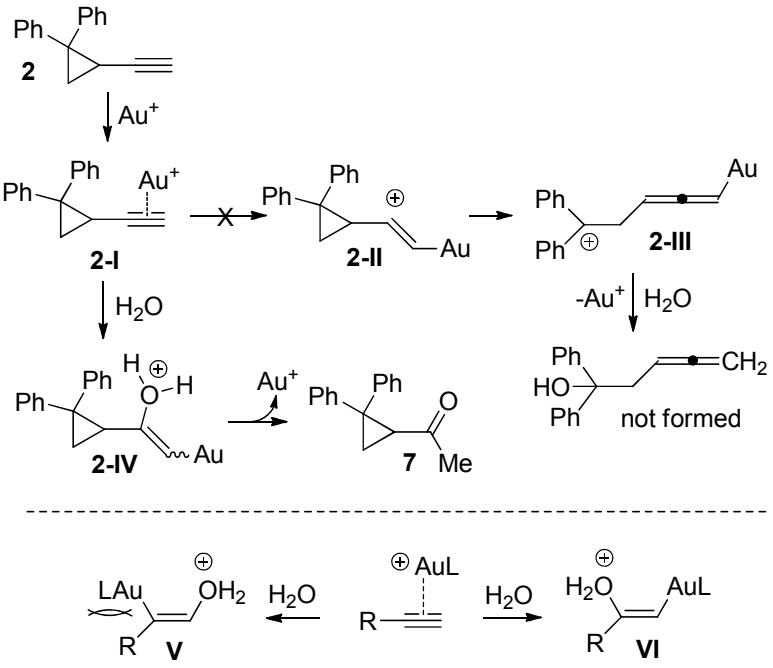


Scheme 5. Hydration of alkyne **2** catalyzed by Au(I), Ag(I), Fe(III) and Hg(II).

$Fe(NTf_2)_3$-catalyzed hydration of **2** forms at the initial stages of reaction allenene **10**, apparently via dehydration of the anticipated highly unstable allenyl alcohol **9**. Although compound **9** was not detected during the progress of the reaction, it is reasonably considered as a reaction intermediate. Allenene **10** gradually undergoes

Friedel-Crafts-type intramolecular cycloisomerization under the reaction conditions into 1-methyl-4-phenylnaphthalene (**11**)[39], which eventually becomes the only reaction product after 16 h (48% isolated yield). The low isolated yield of **11** is associated with its tendency to form side oxidation products at the methyl group under the reaction conditions.

The absence of allene-type side products during the Au-catalyzed hydration of **1** or **2**, is in sharp contrast to the known Bronsted acid-catalyzed procedure[31]; the latter undoubtedly involves the intermediacy of vinyl carbocations such as **1-H$^+$** shown in Scheme 3. Thus, we envision a loose coordination of gold on the triple bond of **1** or **2** (see the case of alkyne **2** in Scheme 6) which does not generate a vinyl carbocation such as **2-II**, followed by nucleophilic attack (syn or anti) on the internal sp-C atom. The

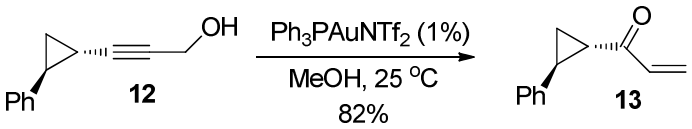


Scheme 6. Mechanistic considerations in the Au$^+$-catalyzed hydration of cyclopropyl alkyne **2**.

reasons of the Markovnikov selectivity might be attributed to the higher electrophilic character of the internal sp-C upon interacting to gold (presumably a slight δ^+ charge not capable of causing skeletal rearrangement to an allene). In addition to this argument, we tentatively propose that steric factors may also play an important role and contribute significantly to the regioselectivity of hydration of terminal alkynes. Thus, nucleophilic attack on the terminal acetylenic carbon atom induces repulsive non-bonding interactions among the ligated Au-C bond and the R group of the reacting terminal alkyne (RC≡CH), as shown in the intermediate **V** at the bottom part of Scheme 6. On the other hand, nucleophilic attack on the internal acetylenic carbon atom (intermediate **VI**) leads to less destabilizing non-bonding interactions. The Ag(I)-catalyzed hydration of **1** and **2** yields significant amounts of allenes (**4** and **8**, respectively), which implies that the internal Csp carbon atom of the alkyne has a pronounced electrophilic character, resembling an open vinyl carbocation after complexation to Ag^+.[40] The Fe(III)-catalyzed hydration reaction of **1** and **2** provides exclusively allene rearrangement products, in accordance with a pure carbocationic character of the intermediate adduct among alkyne and the metal. This trend is also reflected in the $Fe(NTf_2)_3$-catalyzed hydration of internal phenyl-alkyl substituted alkynes which exclusively yields acetophenones[33] (>99% Markovnikov selectivity). Finally, mercury(II) provides idendical to Au(I)-catalysis results. In general, the similarities between the relativistic Au(I) and Hg(II) in catalysis have been pointed out.[41]

A further example which shows the reluctance of a Au^+-bound alkyne, such as **1** or **2**, to undergo cyclopropyl rearrangement into an allene, was shown in the $Ph_3PAuNTf_2$-catalyzed isomerization of the *trans*-(2-phenyl)cyclopropan-1-yl internal alkynol **12** in methanol, which produced after 2h at 25 ^oC cyclopropyl enone **13**[42]

(Scheme 7) in 82% isolated yield via a Meyer-Schuster rearrangement.[43] No allene side products were detected in the crude reaction mixture.



Scheme 7. The Au(I)-catalyzed Meyer-Schuster rearrangement of internal alkynol **12**.

In conclusion, we have shown herein that the Au(I or III) activation of alkynes does not generate vinyl carbocations as intermediates supporting loose metal – π complexes (such as **I** or **II**, Scheme 2), as judged by the lack of allene rearranged products in the hydration or Meyer-Schuster rearrangement of aryl-substituted cyclopropyl alkynes (hypersensitive probes to trace vinyl carbocations). Our findings are in agreement with reported examples of crystal structures of complexes between alkynes and Au^+ where the triple bond acts as a weak electron donor.[44-45] On the other hand, in the Ag(I) or Fe(III) interaction to alkynes a profound vinyl carbocationic character appears in the metal-alkyne complexes as judged by the partial (Ag^+) or exclusive (Fe^{3+}) formation of allene-type rearrangement products from the aryl-substituted cyclopropyl alkynes **1** and **2**.

EXPERIMENTAL SECTION

General: The reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F-254) with UV light as the visualizing method and an acidic mixture of phosphomolybdic acid/cerium(IV) sulfate accompanied by heating of the plate as a developing system. Flash column chromatography was carried out on SiO_2 (silica gel 60, particle size 0.040–0.063 mm) with the specified eluent. NMR spectra

were recorded on a Bruker DPX-300 instrument. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed with a GC–MS QP 5050 Shimadzu single-quadrupole mass spectrometer. High resolution mass spectra (HRMS) were recorded on ESI-Orbitrap mass spectrometer.

Synthesis of cyclopropyl alkynes: Alkynes **1** and **2** were prepared according to known literature protocols (see a schematic presentation in Supporting Information). Internal alkyne **12** was prepared in 67% isolated yield by reacting **1** (0.1 g, 0.75 mmol) with 1.2 equiv of *n*-BuLi (1.6M in hexanes, 0.52 mL) in dry THF at -78 ^{o}C for 20 min, followed by quench with 50% molar excess of paraformaldehyde at 0 ^{o}C for 1 h. (***trans*-2-Ethynylcyclopropyl)benzene (1)**[31]: ^{1}H NMR (300 MHz, $CDCl_3$): 7.27-7.16 (m, 3H), 7.09 (dd, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 2H), 2.29-2.25 (m, 1H), 1.91 (d, J = 2.0 Hz, 1H), 1.54-1.48 (m, 1H), 1.37-1.30 (m, 1H), 1.28-1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.5, 128.4, 126.3, 126.0, 86.2, 64.8, 26.1, 17.4, 10.8. **(2-Ethynylcyclopropane-1,1-diyl)dibenzene (2)**[28]: ^{1}H NMR (300 MHz, $CDCl_3$): 7.43 (d, J = 7.5 Hz, 2H), 7.35-7.15 (m, 8H), 2.22-2.16 (m, 1H), 1.88 (d, J = 2.0 Hz, 1H), 1.72 (dd, J_1 = 5.0 Hz, J_2 = 5.0 Hz, 1H), 1.64 (dd, J_1 = 7.0 Hz, J_2 = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.5, 128.4, 126.3, 126.0, 86.2, 64.8, 26.1, 17.4, 10.8. ***trans*-3-(2-Phenylcyclopropyl)prop-2-yn-1-ol (12)**: ^{1}H NMR (300 MHz, $CDCl_3$): 7.30-7.07 (m, 5H), 4.27 (d, J = 1.5 Hz, 2H), 2.30-2.23 (m, 1H), 1.57-1.50 (m, 1H), 1.55 (br s, 1H, -OH), 1.35-1.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.4, 128.3, 126.1, 125.8, 87.8, 75.0, 51.0, 26.0, 17.4, 11.1; HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}O$+H, 173.0966; Found 173.0960.

Hydration of cyclopropyl alkynes: The hydration of alkynes **1** and **2** as well as the Meyer-Schuster rearrangement of **12** were performed on a 0.1-0.3 mmol scale following known literature protocols.[6,16,32,33,34,43] The products were purified by flash column chromatography using petroleum ether or hexane/ethyl acetate gradients.

Products from the metal-catalyzed hydration of alkynes

***trans*-1-(2-Phenylcyclopropyl)ethanone (3)[46]:** Colorless oil (0.015 g from a 0.1 mmol scale reaction of **1** catalyzed by $Ph_3PAuNTf_2$, 94%). R_f = 0.73 (hexane/EtOAc = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.29-7.20 (m, 3H), 7.10 (dd, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 2H), 2.58-2.50 (m, 1H), 2.30 (s, 3H), 2.27-2.19 (m, 1H), 1.71-1.63 (m, 1H), 1.41-1.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 206.8, 140.3, 128.5, 126.5, 126.0, 32.8, 30.8, 30.0, 19.1.

(1-Methoxypenta-3,4-dien-1-yl)benzene (4)[35]: Colorless oil (0.011 g from a 0.3 mmol scale reaction of **1** catalyzed by $AgSbF_6$, 22%). R_f = 0.65 (hexane/EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.39-7.28 (m, 5H), 5.08 (m, 1H), 4.64 (m, 2H), 4.19 (dd, J_1 = 7.5 Hz, J_2 = 5.5 Hz, 1H), 3.24 (s, 3H), 2.56-2.43 (m, 1H), 2.41-2.30 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 209.2, 141.5, 128.3, 127.6, 126.7, 86.3, 83.5, 74.6, 56.7, 37.1.

5-Methoxy-5-phenylpentan-2-one (5)[36]: Colorless oil (the isolated yield of **5** depends on the reaction time since it is a secondary product deriving from **3**). R_f = 0.41 (hexane/EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.37-7.26 (m, 5H), 4.13 (dd, J_1 = 7.5 Hz, J_2 = 5.5 Hz, 1H), 3.20 (s, 3H), 2.50 (t, J = 7.0 Hz, 2H), 2.11 (s, 3H), 2.06-1.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 208.5, 141.7, 128.4, 127.6, 126.5, 82.8, 56.6, 39.7, 32.0, 29.9.

1-Phenylpenta-3,4-dien-1-ol (1a)[31]: Colorless oil (the isolated yield of **1a** depends on the reaction time since it gradually dehydrates to **6** under the reaction conditions). R_f = 0.25 (hexane/EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.37-7.26 (m, 5H), 5.12 (m, 1H), 4.76 (t, J = 6.5 Hz, 1H), 4.73 (m, 2H), 2.51-2.43 (m, 2H), 2.11 (br s, 1H –OH); ^{13}C NMR (75 MHz, $CDCl_3$): 209.3, 143.4, 128.2, 127.4, 125.6, 85.9, 83.5, 74.9, 73.4, 38.3.

(*E*)-Penta-1,3,4-trien-1-ylbenzene (6)[37]: Colorless oil (the isolated yield of **6** depends on the reaction time since it is a secondary product resulting from the dehydration of **1a**

under the reaction conditions). R_f = 0.70 (hexane/EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.40-7.07 (m, 5H), 6.60 (dd, J_1 = 16.0 Hz, J_2 = 10.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.01 (td, J_1 = 10.0 Hz, J_2 = 6.5 Hz, 1H), 5.01 (d, J = 6.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 212.6, 137.0, 130.1, 128.4, 127.2, 126.0, 123.9, 93.8, 76.4.

1-(2,2-Diphenylcyclopropyl)ethanone (7)[38]: Colorless oil (0.021 g from a 0.1 mmol scale reaction of **2** catalyzed by $Ph_3PAuNTf_2$, 90%). R_f = 0.43 (hexane/EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.32-7.16 (m, 10H), 2.83 (dd, J_1 = 8.0 Hz, J_2 = 6.0 Hz, 1H), 2.29 (dd, J_1 = 6.0 Hz, J_2 = 4.5 Hz, 1H), 2.16 (s, 3H), 1.60 (dd, J_1 = 8.0 Hz, J_2 = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.9, 145.0, 139.4, 129.9, 128.5, 128.4, 127.5, 127.1, 126.6, 42.7, 37.2, 31.3, 21.1.

(1-Methoxypenta-3,4-diene-1,1-diyl)dibenzene (8): Colorless oil (the isolated yield of **8** depends on the reaction time and varies from 35-45% since it gradually decomposes into **10** and **11** during the progress of the reaction). R_f = 0.60 (hexane/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.50-7.25 (m, 10H), 4.82 (m, 1H), 4.55 (td, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 2H), 3.10 (s, 3H), 3.09 (td, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 209.4, 135.0, 132.2, 127.7, 126.3, 84.4, 83.5, 73.9, 50.0, 35.2; HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}O$+H, 251.1436; Found 251.1431.

Penta-1,3,4-triene-1,1-diyldibenzene (10): ^{1}H NMR (300 MHz, $CDCl_3$): 7.45-7.25 (m, 10H), 6.55 (dd, J_1 = 11.0 Hz, J_2 = 1.0 Hz, 1H), 5.95 (td, J_1 = 11.0 Hz, J_2 = 6.5 Hz, 1H), 4.96 (dd, J_1 = 6.5 Hz, J_2 = 1.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 213.7, 142.0, 141.6, 139.3, 130.3, 128.3, 128.2, 127.4, 127.4, 127.3, 122.6, 91.9, 76.1. This compound is an intermediate product in the Fe(III)-catalyzed isomerization of **2** to **11**, and during the progress of the reaction coexists either with **2** (early stages) or with **11** (late stages). As it is isomeric to **2** to **11** and chromatographically inseparable from

them, no HRMS could be recorded. It was however, detected by GC-MS. MS (EI): 218 (M^+, 100%), 203 (63%), 107 (30%), 101 (32%), 94 (27%).

1-Methyl-4-phenylnaphthalene (11)[39]**:** Colorless oil (0.010 g from a 0.1 mmol scale reaction of **2** catalyzed by $Fe(NTf_2)_3$, 48%). R_f = 0.71 (hexane/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): 8.07 (d, J = 9.0 Hz, 1H), 7.57-7.31 (m, 9H), 2.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 141.0, 138.7, 135.2, 133.8, 132.8, 131.7, 130.2, 128.2, 127.0, 126.7, 126.6, 126.2, 125.6, 124.4, 19.6.

***trans*-1-(2-Phenylcyclopropyl)prop-2-en-1-one (13)**[41]: Colorless oil (0.014 g from a 0.1 mmol scale reaction of **12** catalyzed by $Ph_3PAuNTf_2$, 83%). R_f = 0.76 (hexane/EtOAc = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): 7.34-7.11 (m, 5H), 6.51 (dd, J_1 = 17.5 Hz, J_2 = 11.0 Hz, 1H), 6.28 (dd, J_1 = 17.5 Hz, J_2 = 1.0 Hz, 1H), 5.84 (dd, J_1 = 11.0 Hz, J_2 = 1.0 Hz, 1H), 2.62-2.56 (m, 1H), 2.47-2.41 (m, 1H), 1.80-1.74 (m, 1H), 1.49-1.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 198.5, 140.4, 136.8, 128.5, 128.1, 126.6, 126.1, 30.2, 29.6, 19.2.

Acknowledgments: This was supported in part by the ELKE, University of Crete (KA 3823). We thank ProFI (ITE, Heraklion, Greece) for obtaining the HRMS spectra of unknown compounds.

Dedication: Dedicated to professor Michael Orfanopoulos on the occasion of his 65th birthday.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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