

Covalently Bonded Bis(phosphane)gold(I) Cations in a Cross-Linked Phosphazene Polymeric Matrix as Recyclable Supported Catalysts for Thermal and Microwave-Assisted Hydration of Alkynes

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The unexpected finding that the complex $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ (**C1**) catalyses the specific hydration of 1-octyne, (*p*-phenoxyphenyl)acetylene, phenylacetylene, (*p*-chlorophenyl)acetylene and benzylacetylene at 100 °C in the presence of H_2SO_4 and THF or methanol as solvents, specially using microwave radiation, led to the first gold(I) recyclable catalysts for this reaction. The phosphazene polymeric framework of idealised formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_{0.15}\}_n$ (**C2**), and the newly synthesised cyclomatrix material of idealised formula $\{[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6](\text{AuPF}_6)_{3.5}\}_n$ (**C3**), both having cationic $[-\text{Ph}_2\text{P}-\text{Au}^+-\text{PPh}_2-]$

cross-linking sites, catalysed the complete hydration of terminal alkynes at 100 °C and 150 °C and could be used six and four times respectively without significant loss of activity. The mechanism of the catalytic system is based on the initial reversible displacement of one anchoring $\text{O}-\text{C}_6\text{H}_5-\text{PPh}_2$ group from the $[-\text{Ph}_2\text{P}-\text{Au}^+-\text{PPh}_2-]$ cross-linking sites by an alkyne molecule. Using microwave radiation, the hydration of (*p*-phenoxyphenyl)acetylene, phenylacetylene, (*p*-chlorophenyl)acetylene and benzylacetylene can be completed in 5 min to 2 h in the absence of any gold(I) catalyst.

Introduction

Numerous discrete Au^{I} complexes have been studied as catalysts for a variety of organic reactions.^[1] Since the discovery that the cationic species $[\text{AuL}]^+$ (L = phosphane, arsane or phosphite) catalysed the addition of alcohols to alkynes in the presence of an acid as co-catalyst^[2] and the hydration of alkynes using aqueous MeOH as solvent (better in the presence of CO),^[3] many complexes able to liberate monophosphane-gold(I) cations $[\text{AuPPh}_3]^+$ in situ have been found to catalyse the hydration of alkynes in acidic media.^[1e,1f] Recently, the efficient homogeneous hydration of phenylacetylene using Au^{I} catalysts with trisulfonated triphenylphosphane ligands to increase the solubility in aqueous media was reported,^[4] and later, Corma et al. succeeded in designing the first Au^{I} complexes to catalyse the hydration of alkynes in the absence of an acid at room temperature.^[5]

Very few attempts have been made to synthesise supported recyclable Au^{I} catalysts for this reaction. For example, the trisulfonated triphenylphosphane Au^{I} species mentioned above showed a significant drop in activity after three cycles.^[4] Although Wang, Li et al. achieved 90% conversion of phenylacetylene in 7 h using organometallic Au^{I}

complexes periodically attached to mesoporous silica,^[6] no attempts were made to reuse the catalyst. A similar catalytic system has been used for three consecutive cycles of complete hydrothiolation of alkynes in 45 min, but their hydration was not reported.^[7]

Polymers with transition-metal complexes covalently bound to polymeric chains by a convenient spacer^[8] may be useful in the design of new types of catalysts,^[9] and polyphosphazenes,^[10] which are very versatile, have not been sufficiently explored as supports.^[9a,11] Recently,^[12] we reported the synthesis of cross-linked polymeric materials of composition $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_x\}_n$ ($x = 0.15$ or 0.25) having cationic $[-\text{Ph}_2\text{P}-\text{Au}^+-\text{PPh}_2-]$ cross-linking sites. Their idealised structure (Figure 1), which makes them comparable to hybrid inorganic–organic frameworks, is based on the apparently regular distribution of the two phosphazenic units present in the chains as demonstrated for similar co-polyphosphazenes.^[13]

Although, the parent discrete bis(phosphane) complex $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ has been described as a noncatalyst for the hydration of alkynes,^[1e] we have found that this complex is, in fact, very efficient for terminal alkynes in the presence of sulfuric acid, particularly if microwave radiation is used to increase the reaction temperature. Therefore, we have used the insoluble polymeric material $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_{0.15}\}_n$ (**C2**, $x = 0.15$ in Figure 1) as a supported catalyst that can be recycled seven times. To the best of our knowledge this is the first supported Au^{I} recyclable catalyst for the hydration of alkynes.

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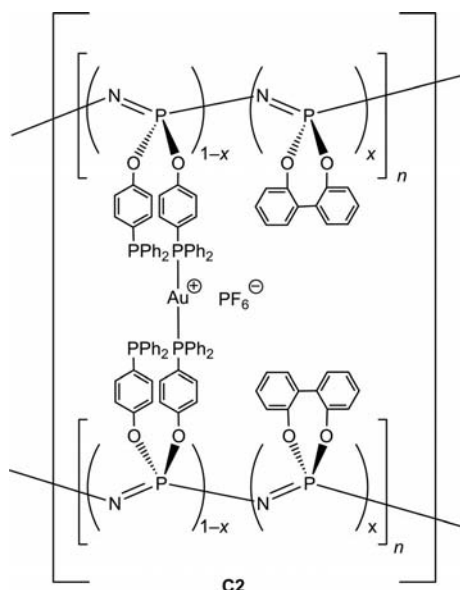
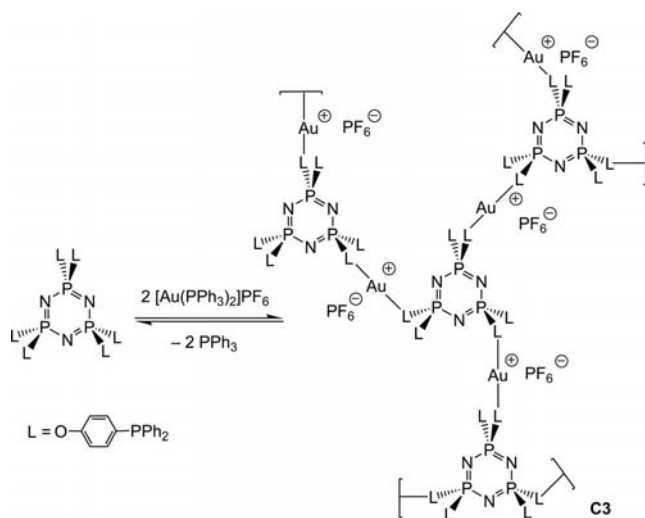


Figure 1. Idealised structure of the polyphosphazene framework **C2**.

We also observed that the new related gold(I) cyclomatrix material, with idealised formula $\{[N_3P_3(OC_6H_4PPh_2)_6]-(AuPF_6)_{0.35}\}_n$ (**C3**) (Scheme 1), easily synthesised by stirring together at room temperature the cyclic hexaphosphane-phosphazene $[N_3P_3(OC_6H_4PPh_2)_6]$ and $[Au(PPh_3)_2]PF_6$, catalyses the same reaction and can also be reused several times.



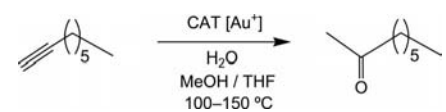
Scheme 1. Synthesis and idealised structure of the cyclophosphazene matrix **C3**.

Results and Discussion

Heating at 100 °C in a sealed tube under N_2 a mixture of 1-octyne and water (excess) in methanol or THF in the presence of $[Au(PPh_3)_2]PF_6$ (**C1**) (ca. 2 mol-% with respect to the alkyne) and H_2SO_4 (ca. 15 mol-%) resulted in 100% conversion to 2-octanone in 12 h (entry 2 of Table 1) as re-

vealed by GC. The hydration also took place at room temperature although very slowly (see Exp. Section). Very little or no conversion was noted in the absence of solvents, or **C1** (entry 3 of Table 1) or sulfuric acid (entry 4 of Table 1). The necessity of a strong acid as a co-catalyst for the hydration of alkynes is well documented and only recently gold(I) complexes have been designed with catalytic activity in the absence of the acid.^[5]

Table 1. Conditions for the hydration of 1-octyne to 2-octanone.



Entry	CAT (mol-% Au ⁺)	H ₂ SO ₄ [mol-%]	T [°C]	Time [h]	Conv. [%]
1 ^[a]	C1 (1)	15	100	16	45
2 ^[a]	C1 (2)	15	100	12	100
3 ^[a]	–	15	100	16	10
4 ^[a]	C1 (2)	–	100	16	6
5 ^[a]	C1 (2)	15	100	1 ^[d]	100
6 ^[b]	C2 (2)	360	100	16	100
7 ^[b]	–	360	100	16	18
8 ^[b]	C2 (2)	360	100	1.75 ^[d]	100
9 ^[c]	C3 (9.5)	15	150	16	100
10 ^[c]	–	15	150	16	25
11 ^[c]	C3 (9.5)	50	150	12	100
12 ^[c]	–	50	150	12	30
13 ^[c]	C3 (9.5)	15	150	10 ^[d]	100
14 ^[c]	C3 (9.5)	50	150	2 ^[d]	100

[a] Using MeOH or THF (0.5 mL) as solvent. [b] Using a mixture THF/MeOH (2.0:0.15 mL). [c] Using a mixture MeOH/THF (2.0:0.1 mL). [d] Using microwave radiation to increase the temperature.

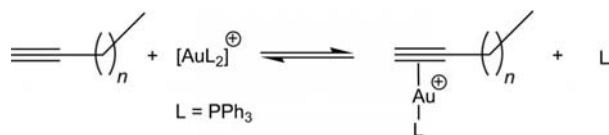
Heating the reaction with microwave radiation, at 100 °C, total conversion was achieved in 1 h (entry 5 of Table 1). Under the same conditions without **C1** the conversion was only 4% but reached 96% in 21 h at 150 °C with 1 mol sulfuric acid per mol of alkyne. It has been previously shown that microwaves are useful in promoting other reactions where alkynes are catalysed by gold complexes.^[16]

Under the same thermal conditions used for 1-octyne, the gold catalyst $[Au(PPh_3)_2]PF_6$ (**C1**) also led to 100% conversion to the corresponding ketones with the terminal alkynes $C_6H_5-CH_2-C\equiv CH$ (10 h), $p-Cl-C_6H_4-C\equiv CH$ (9 h), $C_6H_5-C\equiv CH$ (7 h), and $p-PhO-C_6H_4-C\equiv CH$ (5 h). However, we noted that, using microwaves, these alkynes were completely hydrated without any metal catalyst at 150 °C in methanol with 50% H_2SO_4 in very short times ($C_6H_5-CH_2-C\equiv CH$, 6 h; $p-Cl-C_6H_4-C\equiv CH$, 1 h. $C_6H_5-C\equiv CH$, 30 min; $p-PhO-C_6H_4-C\equiv CH$, 5 min). Again, the sequence was consistent with the degree of activation of the alkyne.

With internal alkynes the hydration with **C1** was not as successful. Moderate conversions were observed with $CH_3CH_2CH_2-C\equiv C-CH_2CH_2CH_3$ at 100 °C and no conversion was noted with $Ph-C\equiv C-Ph$ and $Me-C\equiv C-Ph$ after long time periods (60 h). With the latter alkyne, two ketones were formed at higher temperatures.

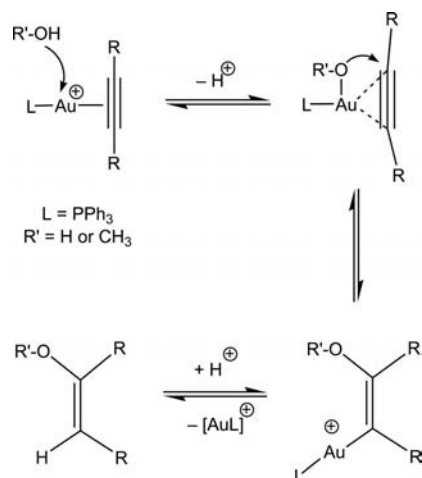
Although not previously reported, the catalytic activity of the complex $[Au(PPh_3)_2]PF_6$ (**C1**) for the hydration of

alkynes is not surprising. It is well known that several gold(I) complexes catalyse this reaction because of the in situ generation of monocoordinated unsaturated $[\text{AuPPh}_3]^+$ cations.^[1c] The appearance of this active species is also expected using **C1** because in the presence of excess of an alkyne the equilibrium shown in Scheme 2 should be easily established. In fact, we have previously reported that terminal alkynyl complexes are able to react with Au^I phosphane complexes in the same manner.^[17]



Scheme 2. Reversible displacement of one phosphane group of the gold(I) cationic complex **C1** by an alkyne.

The coordination of the alkyne to the $[\text{AuL}]^+$ cation activates the hydration according to the plausible mechanism proposed by Corma et al. based on the ketal intermediate.^[5] The attack by methanol in place of water makes the process faster, thus explaining the observed beneficial effects of the presence of methanol in the catalysis (Scheme 3).



Scheme 3. Plausible mechanism for the hydration of alkynes.

The catalytic activity of the complex $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ (**C1**) towards the hydration of alkynes suggested the use of the phosphazene polymeric framework of idealised formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_{0.15}\}_n$ (**C2**), recently described by us,^[12] that has a functionalisation degree (FD) of 0.24 mmol $[\text{Au}^+]$ per gram of material. Using ca. 2 mol-% of $[\text{Au}^+]$, 100% conversion of 1-octyne was observed in 16 h at 100 °C in THF with some methanol and with 3.6:1 excess of H_2SO_4 (entry 6 of Table 1). Using less sulfuric acid the reaction was considerably slower. We noted that with the 3.6:1 excess of sulfuric acid the reaction system was homogeneous. This may be explained by our previous demonstration that the phosphazene chains are easily protonated becoming more exposed to the THF molecules.^[18] Heating at 100 °C with microwaves under the same conditions, 1-octyne was hydrated in 1 h 45 min (entry 8 of Table 1).

The catalyst **C2** could be recovered and reused with success over several cycles. The conversion was very close to 100% for six consecutive cycles, dropping continuously thereafter (Figure 2, a). The recovery was less efficient if diethyl ether was used instead of hexane to wash the recovered material (see Exp. Section). As far as we know, **C2** is the first known recyclable Au^I -supported catalyst for the hydration of alkynes. It seems that the slow hydrolytic degradation of the phosphazene chains,^[18] changes the physical state of the catalyst reducing the mean particle size making it more easily soluble in less polar solvents.

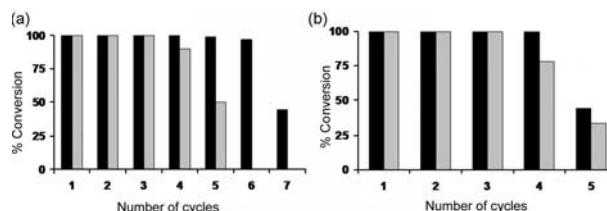


Figure 2. Recycling experiments for the supported $[\text{Au}]^+$ catalyst **C2** (a) and **C3** (b) in the hydration of 1-octyne under thermal (black) and microwave-assisted conditions (grey, see Exp. Section).

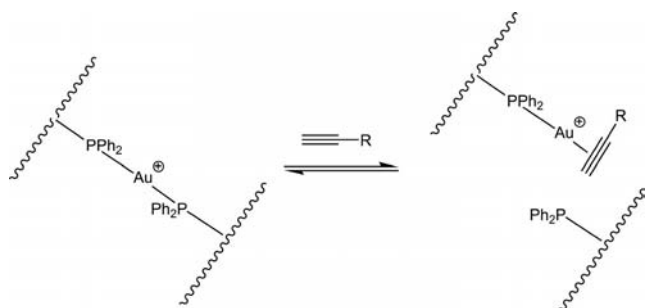
The catalyst **C2** (in ca. 2 mol-% $[\text{Au}^+]$) was also successful with other terminal alkynes. Under the same thermal conditions used for 1-octyne, the alkynes $p\text{-Cl-C}_6\text{H}_4\text{-C}\equiv\text{CH}$ and $\text{C}_6\text{H}_5\text{-C}\equiv\text{CH}$ were hydrated in 1 h 30 min and 1 h 15 min, respectively. However, not surprisingly, little conversion was observed with internal alkynes such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{-C}\equiv\text{C-CH}_2\text{CH}_2\text{CH}_3$ and $\text{Ph-C}\equiv\text{C-Ph}$.

In an attempt to design new recyclable gold-supported catalysts, the polymeric cross-linked cyclomatrix of formula $\{[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6](\text{AuPF}_6)_4\}_n$ (**C3**), chemically related to **C2**, was synthesised by stirring the cyclophosphazene $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6]$ with $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ in THF at room temperature (Scheme 1). The reaction gave a soluble fraction consisting of noncross-linked complexes of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6]$ with $[\text{AuPF}_6]$ and $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ fragments and also led to free PPh_3 (see Exp. Section). Varying the proportions of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6]$ and $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ gave very similar results but with less **C3**. As expected, **C3**, with a FD of 1.17 mmol $[\text{Au}^+]$ /g, also catalysed the hydration of 1-octyne using THF/MeOH/water as solvent and ca. 15 to 50 mol-% H_2SO_4 (entries 9 and 11 of Table 1). The temperature necessary to reach 100% conversion in 12 h was 150 °C (entry 11 of Table 1). At 100 °C the reaction was slower, and this was also so with less sulfuric acid (16 h with 15%, entry 9 of Table 1). Using microwaves at 150 °C the reaction was completed (100%) in 10 h (entry 13 of Table 1) or in 2 h using 50% H_2SO_4 (entry 14 of Table 1). With catalyst **C3** under the same conditions as for 1-octyne without microwave radiation, phenylacetylene and p -chloro-phenylacetylene were 100% hydrated in 12 h.

Recycling experiments showed less efficiency than with **C2**. Better recycling was achieved using less acid (15 mol-%) and no microwaves. The conversion was maintained at ca. 100% for the first three cycles and began to drop to

75% in the fourth reuse (Figure 2, b). Similarly to **C2**, this is caused by the degradation of the average particle size after every catalytic cycle.

The catalytic effect of the polymeric matrices **C2** and **C3** is based on the same effects as for the mononuclear complex **C1** (see Schemes 2 and 3), except for the fact that the liberated phosphane in Scheme 3 remains attached to the polymer matrix in the proximity of the catalytic gold centre (Scheme 4). This is clearly beneficial for the stability of the system, preventing gold species from passing free to the solution. The severe steric hindrance in the region of the active centres explains why less donor and bulky alkynes are not activated by this catalyst.



Scheme 4. Reversible displacement of one anchoring ($-\text{O}-\text{C}_6\text{H}_5-\text{PPh}_2$) group from the $[\text{Au}^+]$ cross-linking sites by an alkyne in **C2** and **C3**.

Moreover, as we have previously demonstrated both experimentally and theoretically,^[13] the acid present in the reaction media is capable of protonating the phosphazene N atoms opening the $\text{P}=\text{N}$ bonds of the chains to the water molecules inducing their slow hydrolysis. The subsequent chain degradation would have a destabilising effect on the solid matrix structure causing its fragmentation affecting the physical state and making the recovery more demanding. This may explain the decrease in the catalytic activity after several cycles imposing a limit on the use of the catalyst.

Conclusions

The complex $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ (**C1**) and the gold(I) phosphazene polymeric frameworks of idealised formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_{0.15}\}_n$ (**C2**) and $\{[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6](\text{AuPF}_6)_{3.5}\}_n$ (**C3**), with cationic $[-\text{Ph}_2\text{P}-\text{Au}^+-\text{PPh}_2-]$ cross-linking sites, catalyse the complete and regiospecific hydration of various terminal alkynes (1-octyne, benzylacetylene, (*p*-phenoxyphenyl)acetylene, (*p*-chlorophenyl)acetylene and phenylacetylene) in 12–22 h at 100–150 °C in the presence of H_2SO_4 and THF or MeOH as solvents. Using microwave radiation, the reaction times are less than 1 h and the activated alkynes can be hydrated without the metal catalyst. The insoluble catalyst **C2** can be recovered and recycled six times with conversion above 90%. **C3** can be recycled three times.

The reaction begins by the reversible displacement of one anchoring $\text{O}-\text{C}_6\text{H}_5-\text{PPh}_2$ group from the $[-\text{Ph}_2\text{P}-\text{Au}^+-$

$\text{PPh}_2-]$ cross-linking sites by an alkyne molecule, and the slow loss of activity is explained by the basicity and chain degradability of the phosphazene by acidic hydrolysis.

Experimental Section

Materials: All reactions were carried out under dry nitrogen. The well-known^[14] $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$ complex was prepared in one step using KPF_6 and $\text{AuCl}(\text{SC}_4\text{H}_8)$ as described below. The material $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_{0.15}\}_n$ (**C2**) was prepared and characterised as described previously.^[12] The molecular weight of the formula unit of **C2** is 3212.2 g/mol, and the functionalisation degree (FD, mmol Au^+ per gram of material) calculated for the idealised composition is $0.5 \times 0.15 / 0.3212 = 0.24$ mmol Au^+/g . The new catalyst $\{[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6](\text{AuPF}_6)_{3.5}\}_n$ (**C3**) (with FD = $3.5 / 0.2995 = 1.17$ mmol Au^+/g), was prepared as described below. The starting cyclic phosphazene $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6]$ was obtained as described elsewhere.^[15] The alkynes were used as received (Aldrich). Sulfuric acid (98 wt.-%, Merck) had a density of 1.84 g/cm³.

General Methods: The IR spectra were recorded with a Perkin–Elmer FT Paragon 1000 spectrometer. Wavenumbers are given in cm^{-1} . NMR spectra were recorded at room temperature with Bruker NAV-400, DPX-300, AV-400 and AV-600 instruments, using CDCl_3 , CD_2Cl_2 , and $[\text{D}_6]\text{DMSO}$ as solvent unless otherwise stated. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR are given in δ relative to TMS. $^{31}\text{P}\{^1\text{H}\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4 . The C,H,N analyses were performed with an Elemental Vario Macro. GC were measured with a Hewlett–Packard HP-6890 using Supelco Beta-Dex™ 120 (30 m, 0.25 mm, 0.25 μm) and Restek RT-Gamma-DexSa (30 m, 0.25 mm, 0.25 μm) columns.

1. Preparation of $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ (C1**):** To a solution of PPh_3 (0.98 g, 3.75 mmol) in THF (30 mL), $[\text{AuCl}(\text{SC}_4\text{H}_8)]$ (0.5 g, 1.56 mmol) and KPF_6 (1.15 g, 6.25 mmol) were added and the suspension was refluxed with stirring for 2 h. The resultant mixture was filtered and concentrated to 10 mL. Diethyl ether was slowly added with stirring to form $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$ as a white precipitate that was washed with diethyl ether and dried in vacuo for 2 h; yield 1.21 g (90%). This procedure avoids the more hazardous TIPF_6 reagent used previously.

2. Preparation of **C3:** A solution of $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ (0.24 g, 0.28 mmol) in THF (10 mL) was added over a stirred solution of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6]$ (0.20 g, 0.14 mmol) in THF (25 mL). A white precipitate was immediately formed. The mixture was stirred at room temperature for 24 h (no changes were observed in the ^{31}P -NMR spectrum of the liquid and no additional precipitate was noted). The mixture was decanted and the solid was washed with THF (3×10 mL) and dried at reduced pressure for 12 h to give **C3** as a white solid (0.19 g, 45.4% yield). Evaporating all the mother liquids a yellow solid was obtained that was extracted with Et_2O (2×15 mL) and dried to give a soluble fraction **SF** (0.12 g, 30% yield), consisting of a mixture of the complexes $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{PPh}_2)_6]$ and AuPF_6 in overall ratio 1:1. Finally, drying the Et_2O gave a residue of pure PPh_3 (0.1 g).

C3: $\text{C}_{108}\text{H}_{84}\text{Au}_{3.5}\text{F}_{21}\text{N}_3\text{O}_6\text{P}_{12.5}$ (2995.35); calcd. C 43.31, H 2.83, N 1.40; found C 41.09, H 2.79, N 2.03 (low found carbon contents are typical of phosphazenes). IR (KBr): $\tilde{\nu} = 3053.0$ (m, $\nu_{\text{C-arom.}}$), 1651.2 (m), 1587.2 (m), 1490.5 (s), 1435.7 (s, $\nu_{\text{C=C-arom.}}$), 1398.8 (s), 1305.3 (vw), 1270.1 (m, $\nu_{\text{PO-C}}$), 1208.0 (vs), 1188.3 (vs), 1163.6 (vs, ν_{PN}), 1096.3 (s, $\nu_{\text{P-OC}}$), 953.4 (s), 832.6 (vs, ν_{PF}), 742.5 (δ_{PNP}), 692.2 (s, $\delta_{\text{C-H, Ph}}$), 557.2 (s, δ_{PF}) cm^{-1} .

Soluble Fraction SF: $C_{108}H_{84}F_6AuN_3O_6P_{10}$ (2140.55): calcd. C 60.60, H 3.96, N 1.96; found C: 57.22, H 3.41, N 1.95. ^{31}P NMR (CD_2Cl_2): δ = 39.5 (broad, m, Au- PPh_3), 30.88 (broad, m, $OC_6H_4PPh_2$ -Au), 9.61 (s, N_3P_3), -144.10 (hp, PF_6) ppm. IR (KBr): $\tilde{\nu}$ = 3053.9 (d, $\nu_{C-arom.}$), 2924.8 (w), 1587.8 (w), 1490.5 (m), 1435.9 (s, $\nu_{C=Carom.}$), 1307.3 (vw), 1269.6 (w, ν_{PO-C}), 1207.1 (s), 1187.6 (s), 1165.2 (vs, ν_{PN}), 1118.2 (m), 1096.4 (m, ν_{P-OC}), 953.8 (s), 883.8 (w), 837.6 (vs, ν_{PF}), 744.1 (m, δ_{PNP}), 693.6 (s), 559.0 (m, δ_{PF}) cm^{-1} .

3. Catalytic Studies: All experiments were carried out in a sealed Young tube under N_2 , with deoxygenated solvents (see the representative example below). The reagents were introduced in the following order: the catalyst, the solvents THF or MeOH or a combination of both; the alkyne, water and H_2SO_4 . The tube was sealed and heated at the desired temperature until all the alkyne is converted into the ketone (100% conversion), as determined by GC. The microwave experiments were carried out with magnetic stirring in a CME-DISCOVERER S-CLASS system setting the maximum power at 150 W and the pressure at 250 psi.

Hydration of 1-Octyne: (M_w 110.2 g/mol, density 0.747 g/cm 3).

a) Thermal Hydration with C1: 1-Octyne (37 μ L, 0.25 mmol), $[Au(PPh_3)_2]PF_6$ (C1) (4 mg, 0.0046 mmol), methanol (0.5 mL), water (0.5 mL, 27.8 mmol), H_2SO_4 (2 μ L, 0.037 mmol). The tube was sealed and heated at 100 °C. After 12 h 100% conversion to 2-octanone was observed.

Note: No conversion took place in the absence of methanol or THF. Using 2 mg of C1 (ca. 1 mol-%) the conversion was 45% in 16 h. Using no C1, conversion was 10% in 16 h. Using no H_2SO_4 , conversion was 6% in 16 h. At room temperature, conversion was 70% in 15 d with 1% of C1. Under the same conditions used for 1-octyne, the alkynes p -PhO- C_6H_4 -C \equiv CH, C_6H_5 -C \equiv CH, p -Cl- C_6H_4 -C \equiv CH, and C_6H_5 -CH $_2$ -C \equiv CH, were hydrated to the corresponding ketones in 5, 7, 9 and 10 h, respectively.

b) Microwave-Assisted Hydration with C1: 1-Octyne (37 μ L, 0.25 mmol), $[Au(PPh_3)_2]PF_6$ (C1) (4 mg, 0.0046 mmol), methanol (0.5 mL), water (0.5 mL), H_2SO_4 (2 μ L, 0.0368 mmol). The tube was heated at 100 °C with microwaves for 1 h. The conversion to 2-octanone was 100%. Identical result was obtained with THF as solvent.

Note: The same experiment excluding the gold catalyst (C1) gave 4% conversion in 1 h. At 150 °C, using methanol and 50 mol-% of H_2SO_4 in the absence of C1, the alkynes p -PhO- C_6H_4 -C \equiv CH, C_6H_5 -C \equiv CH, p -Cl- C_6H_4 -C \equiv CH, and C_6H_5 -CH $_2$ -C \equiv CH, were hydrated in 5 min, 30 min, 1 h, and 6 h, respectively.

c) Thermal and Microwave-Assisted Hydration with C2: 1-Octyne (74 μ L, 0.5 mmol), C2 (40 mg, 0.01 mmol $[Au^+] = 1.92$ mol-% with respect to the alkyne), THF (2 mL), methanol (0.15 mL), water (0.15 mL, 8.3 mmol), H_2SO_4 (98 μ L, 1.8 mmol). The addition of the acid caused the catalyst to go into solution. The mixture was heated at 100 °C for 16 h (100% conversion).

Note: In the experiments excluding the catalysts C1, conversion was less than 18% in 16 h. Under the same thermal conditions used for 1-octyne, the alkynes p -Cl- C_6H_4 -C \equiv CH and C_6H_5 -C \equiv CH were hydrated in 1 h 30 min and 1 h 15 min, respectively. Using microwave radiation for the heating, 1-octyne was completely hydrated in 1 h 45 min. As noted above, the other alkynes can be hydrated in much shorter times in the absence of the gold(I) catalyst.

d) Recovery of the Catalyst C2 for Further Use: The reaction mixture was concentrated to 1/3 of its volume. Then, water (10 mL) and CH_2Cl_2 (2.5 mL) were added and, after stirring, the aqueous layer was removed. The organic layer was washed with water

(2 \times 5 mL) and dried. The solid residue was washed with diethyl ether (2 \times 5 mL) and dried in vacuo for reutilisation in situ. After the 5th cycle, the material began to be slightly soluble in diethyl ether, so n -hexane was used instead. The absence of any residual ketones from the previous uses was always previously checked by GC. Conversion was 100% in the first five cycles, 97% in the 6th and 90–45% from the 7th cycle. In the microwave experiments, recovery was less successful (three cycles with 100%, and 90–50% thereafter).

e) Thermal and Microwave-Assisted Hydration with C3: 1-Octyne (18 μ L, 0.125 mmol), C3 (10 mg = 0.0117 mmol $[Au^+] = 9.5$ mol-% with respect to the alkyne), methanol (2 mL), water (20 μ L, 1.11 mmol), THF (100 μ L) and H_2SO_4 (1.0 μ L, 0.017 mmol). The mixture was heated at 150 °C for 16 h (conversion 100%). Recuperation and reuse was performed as for C2. 100% conversion was observed in three cycles dropping to 75% in the 4th cycle.

Note: Under the same thermal conditions used for 1-octyne, the alkynes p -Cl- C_6H_4 -C \equiv CH and C_6H_5 -C \equiv CH were completely hydrated in 12 h. Using microwave radiation at 150 °C the reaction was completed (100%) in 10 h or in 2 h using 50 mol-% of H_2SO_4 .

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