Homogenous Catalysis with Gold: Efficient Hydration of Phenylacetylene in Aqueous Media

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A variety of gold(I) complexes containing the water-soluble phosphine ligands TPPMS, TPPDS, and TPPTS (mono-, di-, and tri-sulfonated triphenylphosphine, respectively) were tested as catalysts for the hydration of phenylacetylene in aqueous media. The gold(I) alkynyl complexes [AuC≡CR(TPPTS)] (where R = ^{t}Bu and 3-thiophenyl) give the highest ever reported turnover frequencies (1000 and 1060 h^{-1}, respectively) for the hydration of phenylacetylene under optimum conditions (0.1 mol % catalyst loading, 10 mol % H_2SO_4, 1 h reflux in 5:1 MeOH/H_2O). The hydration of phenylacetylene can also be carried out using only water and reaction medium, which allows recycling of the gold catalyst without significant drop of activity for at least three cycles. DFT calculations were used to compare relative energies of possible intermediates involved in the catalytic cycle.

Introduction

Even though gold was declared "catalytically dead" 11 years ago,[1] the successful use of gold compounds in homogeneous catalysis has since been the subject of an ever increasing number of publications.[2] Initially gold salts such as $AuCl_3$, $Na[AuCl_4]$, or $HAuCl_4$ were employed as catalysts but were later replaced by gold complexes including [AuCl(PPh_3)], [AuMe(PPh_3)], and [Au(NO_3)(PPh_3)]. Using these types of gold catalysts, a variety of organic transformations including asymmetric aldol reactions,[3−7] diboration of vinylarenes,[8] dimerization of trialkylstannanes,[9] carbonylation of olefins[10] and amines,[11,12] C−C and C−O bond-forming reactions,[13−18] and oxidation of sulfides[19] and thioethers[20] have been reported. The hydration of terminal alkynes represents an environmentally benign route to form C−O bonds from readily available hydrocarbon sources, and thus there has been considerable interest in the development of efficient protocols for this process. To date, gold(I) complexes such as [AuMe(PPh_3)] (in the presence of an acid co-catalyst) have been found to be among the most active catalysts for the addition of nucleophiles to alkynes.[21−25] On the basis of spectroscopic evidence and computational data, a mechanism has been proposed in which the catalytically active species is considered to be $[AuP]^+$, derived from metal−carbon bond cleavage of the [AuMe(PPh_3)] pre-catalyst.[23]

The field of aqueous catalysis, i.e., the ability to carry out important organic transformations in water has received considerable attention over the past 10 years. One major limitation is that many active metal catalysts are either insoluble and/or unstable in an aqueous environment. A key strategy to overcome this problem has been the development of water-soluble ligands, in particular water-soluble phosphines. The successful industrial application of the water-soluble rhodium complex [RhH(CO)(TPPTS)$_3$] (TPPTS = trisulfonated triphenylphosphine sodium salt) in the Rhurchemie/Rhône-Poulenc hydroformylation process is one example for green chemistry with an organometallic catalyst carried out on a scale of greater than 600 000 tons per year.[26] We have recently reported the preparation of water-soluble and water-stable organometallic complexes of gold(I),

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Scheme 1

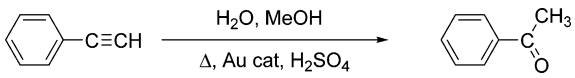

Table 1. Hydration of Phenylacetylene Using [AuCl(P)] and[AuC_6F_5(P)] Catalysts[a]

catalyst	acid	cat. loading (mol %)	time (h)	conversion (%)[b]	TOF (h^{-1})
[AuCl(TPPMS)]	−	2	1.5	5	2
[AuCl(TPPDS)]	−	2	1.5	31	10
[AuCl(TPPTS)]	−	2	1.5	74	25
[AuCl(TPPMS)]	H_2SO_4	2	1.5	42	14
[AuCl(TPPDS)]	H_2SO_4	2	1.5	59	20
[AuCl(TPPTS)]	H_2SO_4	2	1.5	100	33
[AuCl(TPPTS)]	H_2SO_4	1	0.5	74	148
[AuCl(TPPTS)]	H_2SO_4	0.5	0.5	53	212
[AuCl(TPPTS)]	H_2SO_4	0.1	1.5	48	320
[AuC_6F_5(TPPMS)]	H_2SO_4	2	1.5	77	26
[AuC_6F_5(TPPDS)]	H_2SO_4	2	1.5	80	27
[AuC_6F_5(TPPTS)]	H_2SO_4	2	1.5	100	33
[AuC_6F_5(TPPTS)]	H_2SO_4	1	1.5	100	67
[AuC_6F_5(TPPTS)]	H_2SO_4	0.5	1.5	77	103
[AuC_6F_5(TPPTS)]	H_2SO_4	0.1	1.5	2	13
[Au(OTf)(TPPTS)]	H_2SO_4	0.1	1.5	64	427
[Au(O_3SMe)(TPPTS)]	H_2SO_4	0.1	1.5	58	387

[a] Reaction conditions: 0.5 mmol phenylacetylene, 5 mL MeOH, 1 mL H_2O at reflux temperature. [b] Conversion to phenyl methyl ketone determined by GC-MS.

gold(II), and gold(III) containing mono, di, and tri-sulfonated triphenylphosphine ligands denoted as TPPMS, TPPDS, and TPPTS, respectively.[27,28] In pursuing our continuous interest in gold catalysis in aqueous media,[29] we examined the catalytic activity of some new water-soluble gold(I) derivatives in the addition of water to the unactivated terminal alkyne phenylacetylene. The results of this study are presented here.

Results and Discussion

1. Preparation of Gold(I) Complexes. The gold(I) complexes [AuCl(**P**)] and [AuC_6F_5(**P**)] (hereafter and throughout this article **P** shall denote TPPMS, TPPDS, and TPPTS sodium salts) were easily prepared in high yields by reacting the appropriate phosphine with equimolar quantities of [AuCl(tht)] or [AuC_6F_5(tht)], respectively. All new complexes were fully characterized by spectroscopic and analytical techniques as detailed in the Experimental Section. These six complexes are soluble and stable in water; their solubilities range from 38 g/L for [AuCl(TPPMS)] to 1132 g/L and 1000 g/L for the chloro- and pentafluorophenyl TPPTS complexes, respectively.

2. Hydration of Phenylacetylene with [AuCl(P)] and [AuC_6F_5(P)]. Initially we examined the hydration of phenylacetylene (Scheme 1) in a 5:1 MeOH/H_2O mixture using [AuCl(**P**)] and [AuC_6F_5(**P**)] as catalysts both with and without addition of H_2SO_4 as co-catalyst (Table 1).

These results show that the TPPTS complexes always give higher conversions and turnovers, both in the absence and presence of the sulfuric acid co-catalyst, when compared to the TPPDS and TPPMS derivatives. The pentaflourophenyl complexes have similar conversions and turnovers than their chloro analogues; however, at lower catalyst concentrations [AuC_6F_5(TPPTS)] performs much poorer than [AuCl(TPPTS)]. This may be explained by the fact that the relatively strong aryl−carbon−gold bond is cleaved only slowly at this acid concentration (10 mol %), and thus only a small amount of catalytically active [Au(TPPTS)]$^+$ is formed. On the basis of these findings we focused our attention in subsequent experiments on the study of only the TPPTS derivatives. The TPPTS gold(I) complexes containing the weakly coordinated TfO^- and $MeSO_3^-$ ligands gave the highest turnover frequencies under these conditions, again providing further evidence that the [Au(TPPTS)]$^+$ cation plays a key role in this process. Since the mechanism proposed by Teles[23] and Schmidbaur[25] involves π-coordination of the alkyne to the [AuP]$^+$ cation as the second step of the catalytic cycle, we wished to study gold(I) alkynyl complexes as catalysts for the hydration of phenylacetylene. Alkynyl gold(I) compounds are easily synthesized under aerobic conditions and, furthermore, by varying the alkyne it is possible to prepare a library of different alkynyl gold(I) complexes and to study and compare their catalytic activity. For this study we chose a variety of alkynes with different steric, electronic, and solubility properties as illustrated in Scheme 2.The [AuC≡CR(TPPTS)] complexes were prepared in excellent yields by reaction of the chlorogold(I) complex [AuCl(TPPTS)] with an excess of alkyne in the presence of base.

3. Hydration of Phenylacetylene with [AuC≡CR(TPPTS)] Complexes. In order to optimize reaction conditions for the addition of H_2O to phenylacetylene, we carried out a series of experiments in which the phosphine ligand, the type and amount of acid co-catalyst, as well as the alkyne unit (R) was varied.

In order to determine the optimum conditions we initially chose the 1-hexenylgold(I) complex [Au(C≡CC_4H_9)(TPPTS)] as suitable test catalyst for the optimization experiments. Both the type and concentration of the acid co-catalyst affects the performance of the gold catalyst as can be seen in Tables 2 and 3.

It can be seen that acids which are able to cleave the Au−C bond to generate [Au(TPPTS)]$^+$ in the presence of a weakly coordinating anions give high conversions and reasonably high turnovers, with H_2SO_4 being the most effective co-catalyst under these conditions. Acetic acid is completely inactive, probably because the acid is not strong enough to cleave the gold−carbon bond. The fact that HCl is also completely inactive seems counterintuitive at first, since its activity should be similar to that of [AuCl(TPPTS)]. However, examination of the dissociation process shown in Scheme 3, which is very likely to occur in a polar H_2O/MeOH mixture, suggests that in the presence of large excess of chloride the equilibrium will be shifted to the left, and thus no catalytically active [Au(TPPTS)]$^+$ species can be present in solution.

In order to determine the optimal acid concentration, the amount of acid was varied from 2 to 20 mol % with all other variables (type of alkyne and phosphine, reaction time, and catalyst concentration) being fixed. The results show that as the acid concentration is increased, both conversions and turnovers increase, peaking at a concentration of 10 mol % and then dropping again. From these results it was concluded that H_2SO_4 at a concentration of 10 mol % was the most active co-catalyst. As mentioned above (Table 1), the TPPTS derivatives were the most active catalysts in the chloro and pentaflourophenyl series; the same trend is also true in the 1-hexenylgold series, in which the TPPTS derivative is again the most active. Subsequently, the catalytic activity of a library of TPPTS gold(I) alkynyl complexes was examined (Table 3). It should be noted at this point that we observed no product formation if only 10 mol % sulfuric acid (without Au catalyst) was used in the reaction. Recent reports show that in some cases simple

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Scheme 2

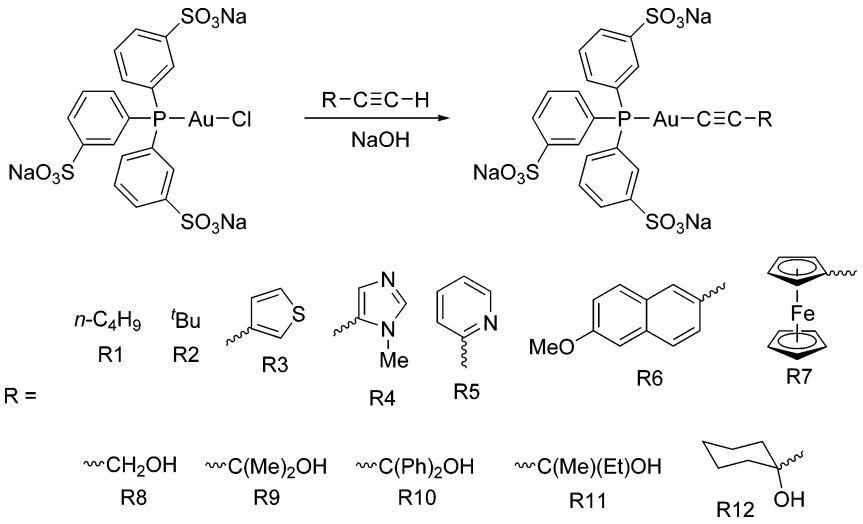

Table 2. Hydration of Phenylacetylene Using [Au(C≡CC$_4$H$_9$)(TPPTS)] with Different Acid Co-Catalysts[a]

acid	conversion (%)[b]	TOF (h^{-1})
HCl	0	0
CH_3COOH	0	0
HPF_6	13	26
HBF_4	28	56
CF_3COOH	37	74
CF_3SO_3H	44	88
H_2SO_4	50	100

[a] Reaction conditions: 0.5 mmol phenylacetylene, 1 mol % catalyst loading, 10 mol % acid, 5 mL MeOH, 1 mL H_20 at reflux temperature for 0.5 h. [b] Conversion to phenyl methyl ketone determined by GC-MS.

Brønsted acids can efficiently catalyze the addition of O−H bonds to olefins even in the absence of metal salts.[30,31]

While no general structure−activity relationship can be derived from this data, there are some significant results to point out. The alkyl-substituted derivatives (R1 = *n*-C_4H_9 and R2 = ^{t}Bu) show very high catalytic activity. In particular, the alkynyl complexes [AuC≡CR2(TPPTS)] and [AuC≡CR3(TPPTS)] (R2 = ^{t}Bu, R3 = 3-thiophenyl) give very high turnovers (1000 and 1060 h^{-1}, respectively) at 0.05 and 0.1 mol % catalyst loading, respectively. These results are the highest ever observed for the hydration of phenylacetylene using gold catalysts. The group of Tanaka previously reported a turnover frequency of 490 h^{-1} using 0.2 mol % [AuMe(PPh_3)] in the presence of CF_3SO_3H for the same reaction.[24] Gold(I) catalysts containing alkynes with polar substituents (R8−R12) give moderate to reasonable conversions with low turnovers. Altering the electronic or steric properties of the alkyne (R4−R7) does not lead to significant improvement of catalytic activity. The results also illustrate that the stability of the alkyne stabilized [Au(η^2-HC≡CR)(TPPTS)]$^+$ cations also plays an important role in this catalytic process. If [Au(TPPTS)]$^+$ on its own was the sole catalytically active species here, one would not observe such a wide range of catalyst performance results.

4. Hydration of Other Alkynes Using [Au(C≡C^{t}Bu)(TPPTS)] and [Au(C≡C−3-C_4H_3S)(TPPTS)] Catalysts. As can be seen from Table 3, the most catalytically active gold species in the hydration of phenylacetylene were [Au(C≡C^{t}Bu)(TPPTS)] and [Au(C≡C−3-C_4H_3S)(TPPTS)]. In order to examine the scope of the reaction with these two catalysts we

Table 3. Hydration of Phenylacetylene with Various Gold(I) Alkynyl Complexes as Catalysts[a]

catalyst[b]	cat. loading (mol %)	time (h)	conversion (%)[c]	TOF (h^{-1})
[AuC≡CR1(TPPTS)]	1	0.5	50	60
			90 (1.5 h)	
	0.5	0.5	23	116
			87 (1.5 h)	
	0.1	0.5	1	80
			12 (1.5 h)	
[AuC≡CR2(TPPTS)]	1	0.5	100	200
	0.5	0.5	100	400
	0.1	0.5	50	1000
			86 (1.5 h)	
	0.05	0.5	20	667
			50 (1.5 h)	
	0.025	0.5	1	453
			17 (1.5 h)	
[AuC≡CR3(TPPTS)]	1	0.5	100	200
	0.5	0.5	100	400
	0.1	0.5	53	1060
			99 (1 h)	
	0.05	0.5	15	533
			40 (1.5 h)	
	0.025	0.5	1	133
			5 (1.5 h)	
[AuC≡CR4(TPPTS)]	1	0.5	1	4
			6 (1.5 h)	
[AuC≡CR5(TPPTS)]	1	0.5	65	67
			100 (1.5 h)	
[AuC≡CR6(TPPTS)]	1	0.5	3	15
			23 (1.5 h)	
[AuC≡CR7(TPPTS)]	1	0.5	11	35
			52 (1.5 h)	
[AuC≡CR8(TPPTS)]	1	0.5	42	55
			82 (1.5 h)	
[AuC≡CR9(TPPTS)]	1	0.5	10	40
			60 (1.5 h)	
[AuC≡CR10(TPPTS)]	1	0.5	60	51
			76 (1.5 h)	
[AuC≡CR11(TPPTS)]	1	0.5	2	8
			12 (1.5 h)	
[AuC≡CR12(TPPTS)]	1	0.5	100	200
	0.5	0.5	28	108
			81 (1.5 h)	
	0.1	0.5	0	0

[a] Reaction conditions: 0.5 mmol phenylacetylene, 10 mol % H_2SO_4, 5 mL MeOH, 1 mL H_20 at reflux temperature. [b] For a definition of the R groups refer to Scheme 2. [c] Conversion to phenyl methyl ketone determined by GC-MS.

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Scheme 3

$$[AuCl(TPPTS)] \rightleftharpoons [Au(TPPTS)]^+ + Cl^-$$

studied the hydration of a variety of other alkynes with those two gold complexes (Table 4).

The results show that the introduction of substituents on the aromatic ring has a marked effect on the reactivity. For example, introduction of electronegative halogen substituents in the *para* position causes the conversions and turnover numbers to drop dramatically, while a methoxy substituent only reduces conversion and turnovers slightly. The linear alkyne 1-octyne shows very conversions and turnovers. Under these reactions conditions nonterminal, internal alkynes do not react at all, as exemplified by PhC≡CMe. The same reactivity trends are observed for both gold catalysts; however [Au(C≡C−3-C_4H_3S)(TPPTS)] seems to be the faster catalyst. In order to gain some kinetic information about both gold catalysts we monitored the conversion of phenylacetylene over time. The kinetic plot is shown in Figure 1.

It can be seen that for both catalysts 100% conversion is reached after a given period of time. In this, the two catalysts show different behavior. The gold complex [Au(C≡C−3-C_4H_3S)(TPPTS)] is almost twice as fast as [Au(C≡C^{t}Bu)-(TPPTS)] in catalyzing this reaction.

5. Hydration of Phenylacetylene in Water. The results described so far were carried out in the presence of MeOH as co-solvent. Ideally, it would be advantageous to be able to carry out the hydration of phenylacetylene in pure water, especially given that the gold catalysts studied in this work are soluble in water. In addition, use of pure water as reaction medium would allow the possibility of catalyst recycling by simple removal of the organic product from the reaction mixture by solvent extraction. The catalytic activity of the two most active gold(I) alkynyl catalysts [AuC≡CR(TPPTS)] (R2 = ^{t}Bu and R3 = 3-thiophenyl) was studied using pure water as reaction medium (Table 4). Upon completion of the reaction, the organic product was removed by extraction with CH_2Cl_2, and the aqueous phase (containing the gold catalyst) was used for a subsequent reaction with fresh alkyne.

The results show that for both catalysts conversions and turnovers in pure water are less when compared to those observed in the H_2O/MeOH mixture. However, it can also be seen that catalyst recycling is indeed feasible; conversions and turnovers drop only slightly from run to run. The aqueous phase was analyzed for gold (using ICP atomic emission spectrometry) for each run (Table 5) to see if any catalyst is leached. Indeed, it can be seen that the gold concentration decreases from run to run, dropping from the initial concentration of 19.69 to 12.10 ppm after the last run. These results explain that catalyst leaching from the aqueous phase is the reason for the observed reduction of catalytic activity from run to run. It is important to note here that the pH of the aqueous phase remained a constant 1.62 for each run so that a change of acid concentration can be excluded as a factor in the decreasing catalytic activity from run to run. To the best of our knowledge, these results are the first reports of the use of water-soluble gold(I) complexes as catalysts for the hydration of phenylacetylene in water with the possibility of catalyst recycling.

6. Computational Studies. Previous computational studies of the hydration of alkynes using gold(I) catalysts have shown that the initial step involves formation of a $[Au(P)]^+$ cation, which is then stabilized by a π-coordinated alkyne.[23] Among the complexes in this study, the alkynyl derivative containing a 3-thiophenyl substituent was the most active catalyst under the conditions tested. In order to shed some light on why this may be the case we computed the relative stabilities of the cation $[Au(H_3TPPTS)(HC{\equiv}CR3)]^+$ (R3 = 3-thiophenyl) in with the alkyne is either π-coordinated (η^2) or acting as *S*-donor ligand. Interestingly, the π-coordinated isomer is 11.4 kcal/mol more stable (in the gas phase) than the *S*-coordinated isomer (Figure 2).

Similarly, π-coordination of phenylacetylene or ^{t}BuC≡CH to $[Au(H_3TPPTS)]^+$ was computed to be exothermic by 29.8 and 29.5 kcal/mol, respectively. Gas-phase calculations and solution chemistry, in particular that of charged species in aqueous media, are two different stories; however, the computational results here are consistent with previous computed mechanistic data. Under the conditions here, in this TPPTS system too, initially the $[Au(TPPTS)]^+$ cation is formed, which is then stabilized by a π-coordinated alkyne. With the computational (and experimental) data available at this point, we have no explanation as to exactly why the gold(I) complexes bearing the thiophenyl- and ^{t}Bu-substituted alkynes are so much more active catalysts than the other alkynyl complexes under investigation, given that energetically the first reaction intermediates (i.e., the alkyne stabilized Au TPPTS cations) are energetically quite similar. Further work to attempt to resolve this question is currently in progress.

Conclusions

We have shown that water-soluble gold(I) alkynyl complexes with suitable substituents are highly active catalysts for the hydration of phenylacetylene in both a H_2O/MeOH mixture and also in water alone. In the latter system, the catalyst containing aqueous phase can be recycled at least three times with only a slight drop in conversion and turnover frequency. The turnover numbers for the two most active catalysts presented here (1000 and 1060 h^{-1}) are the highest ever reported for the hydration of phenylacetylene using gold catalysts.

Experimental Section

General Information. ^{1}H, and ^{31}P{^{1}H} NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer. Chemical shifts are quoted relative to external TMS (^{1}H) and 85% H_3PO_4 (^{31}P); coupling constants are reported in Hz. FAB mass spectra were measured on a VG Autospec spectrometer in positive ion mode using NBA as matrix. TPPMS,[32] TPPDS,[33] [AuCl(tht)],[34] and $[AuC_6F_5(tht)]$[34] were prepared by published procedures. A sample of TPPTS was kindly provided by European Oxo GmbH. All other reagents and solvents were obtained from commercial sources and used as received.

Computational Details. Theoretical calculations were performed using the DFT method, specifically functional PBE,[35] incorporated in the program package Priroda,[36,37] In the PBE calculations relativistic Stevens−Basch−Krauss (SBK) effective core potentials (ECP) optimized for DFT calculations have been used.[38−40] The

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Table 4. Hydration of Various Alkynes Using [Au(C≡C^{t}Bu)(TPPTS)] and [Au(C≡C−3-C_4H_3S)(TPPTS)] as Catalysts[a]

		[Au(C≡C^{t}Bu)(TPPTS)]		[Au(CC≡3-C_4H_3S)(TPPTS)]	
alkyne	cat. loading (mol %)	conversion (%)[b]	TOF (h^{-1})	conversion (%)[b]	TOF (h^{-1})
PhC≡CH	0.1	58	580	100	1000
C_4H_3S-3-C≡CH	0.1	14	140	33	330
$CH_3(CH_2)_5C$≡CH	0.1	80	800	97	970
$CH_3(CH_2)_5C$≡CH	0.05	45	900	75	1500
4-BrC_6H_4C≡CH	0.1	8	80	8	80
4-ClC_6H_4C≡CH	0.1	9	90	20	200
4-MeC_6H_4C≡CH	0.1	41	410	59	590
4-$MeOC_6H_4C$≡CH	0.1	87	870	90	900
PhC≡CMe	0.1	0	0	0	0

[a] Reaction conditions: 0.5 mmol alkyne, 10 mol % H_2SO_4, 5 mL MeOH, 1 mL H_20 1 h at reflux temperature. [b] Conversions determined by GC-MS.

Table 5. Hydration of Phenylacetylene in Water and Catalyst Recycling[a]

catalyst	conversion (%)	TOF (h^{-1})	Au content in aqueous phase (ppm)[b]
[AuC≡CR2(TPPTS)]	41	410	
second run	33	330	
third run	25	250	
[AuC≡CR3(TPPTS)]	54	540	15.15
second run	43	430	12.25
third run	31	310	12.10

[a] Reaction conditions: 0.5 mmol phenylacetylene, 0.1 mol % catalyst loading, 10 mol % H_2SO_4, 5 mL H_20 1 h at 90 °C. [b] Determined by ICP atomic emission spectrometry after each run.

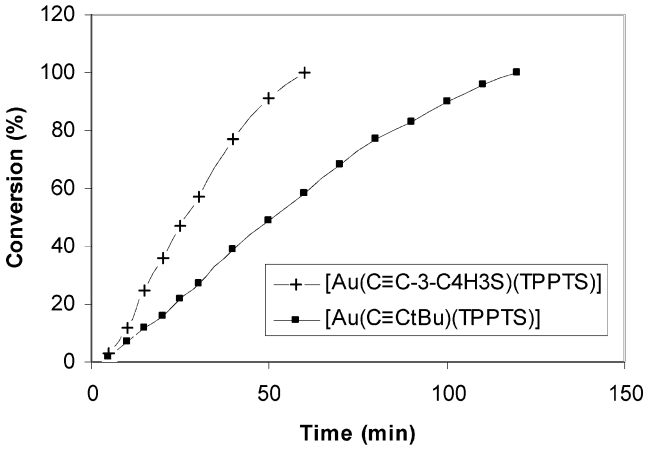

Figure 1. Kinetic plot showing the conversion of phenylacetylene over time. Reaction conditions as described in the footnote of Table 3.

basis set was 311-split for main group elements with one additional polarization p-function for hydrogen and two additional polarization d-functions for the heavier elements. Full geometry optimization was performed without constraints on symmetry. All minima were checked for the absence of imaginary frequencies.

Preparation of [AuCl(P)] (P = TPPMS, TPPDS, and TPPTS). To a solution of [AuCl(tht)] (417 mg, 1.3 mmol) in (70 mL) MeOH was added the phosphine (1.3 mmol). After being stirred for ca. 40 min, the solution was filtered through Celite, and the filtrate was concentrated in vacuum to ca. 3 mL. Addition of Et_2O precipitated the colorless complexes which were isolated by filtration, washed with Et_2O, and dried in vacuum.

[AuCl(TPPMS)]. Colorless solid, 82% yield. ^{1}H NMR (D_2O): δ 6.92−7.58 (m, 12 H, Ph_2P, *H*5, *H*2), 7.65 (d, J = 12.3 Hz, 1 H, *H*4), 7.76 (d, J = 7.5 Hz, 1 H, *H*6). ^{31}P{^{1}H} NMR (D_2O): δ 34.12. FAB-MS: 597 $[M]^+$, 561 $[M - Cl]^+$. Analysis calcd for $C_{18}H_{14}O_3$-ClPSAuNa·H_2O (613.90) % C 35.18, H 2.63, S 5.21; found % C 34.85, H 2.37, S 4.76.

[AuCl(TPPDS)]. Colorless solid, 87% yield. ^{1}H NMR (D_2O): δ 7.36−7.81 (m, 9 H, PhP, *H*6, *H*5), 7.89 (d, J = 13.2 Hz, 2 H, *H*4), 7.96 (d, J = 7.3 Hz, 2 H, *H*2). ^{31}P{^{1}H} NMR (D_2O): δ 32.97. FAB-MS: 699 $[M]^+$. Analysis calcd for $C_{18}H_{13}O_6ClPS_2AuNa_2$·$3H_2O$ (751.94) % C 28.73, H 2.55, S 8.50; found % C 28.35, H 2.25, S 8.13.

[AuCl(TPPTS)]. Colorless solid, 93% yield. ^{1}H NMR (D_2O): δ 7.63−7.76 (m, 6 H, *H*6, *H*5), 7.94−8.06 (m, 6 H, *H*2, *H*4). ^{31}P-{^{1}H} NMR (D_2O): δ 33.46. FAB-MS: 800 $[M]^+$. Analysis calcd for $C_{18}H_{12}O_9ClPS_3AuNa_3$·$^1/_2H_2O$ (808.85) % C 26.70, H 1.62, S 11.86; found % C 28.86, H 1.98, S 11.90.

Preparation of [AuC$_6$F$_5$(P)] Complexes. A mixture of [AuC$_6$F$_5$-(tht)] (0.08 g, 0.18 mmol) and the appropriate phosphine (0.18 mmol) in MeOH (5 mL) was stirred for ca. 45 min. The resulting solution was passed through Celite, and the filtrate concentrated in vacuum to ca. 3 mL. Addition of hexanes precipitated the product, which was isolated by filtration, washed with Et_2O, and dried.

[AuC$_6$F$_5$(TPPMS)]. Colorless solid, 66% yield. ^{1}H NMR (D_2O): δ 7.30−7.70 (m, 12 H, *H5*, *H6*, Ph_2P), 8.06−8.06 (m, 2 H, *H*2, *H*4). ^{31}P{^{1}H} NMR (D_2O): δ 43.50. ^{19}F NMR (D_2O): δ −115 (m, *o*-F), −158 (t, J = 10.7 Hz, *p*-F), −162 (m, *m*-F). Analysis calcd for $C_{24}H_{14}O_3F_5PSAuNa$·H_2O (745.99) % C 38.62, H 2.16, S 4.30; found % C 38.16, H 2.23, S 3.99.

[AuC$_6$F$_5$(TPPDS)]. Colorless solid, 85% yield. ^{1}H NMR (D_2O): δ 7.21−7.51 (m, 9 H, PhP, *H*6, *H*5), 7.55 (d, J = 12.8 Hz, 2 H, *H4*), 7.76 (d, J = 7.4 Hz, 2 H, *H2*). ^{31}P{^{1}H} NMR (D_2O): δ 44.10. ^{19}F NMR (D_2O): δ −115 (m, *o*-F), −158 (t, J = 10.7 Hz, *p*-F), −162 (m, *m*-F). Analysis calcd for $C_{24}H_{13}O_6F_5PS_2AuNa_2$·$^1/_2H_2O$ (838.93) % C 34.33, H 1.68, S 7.62; found % C 34.11, H 1.60, S 7.68.

[AuC$_6$F$_5$(TPPTS)]. Colorless solid, 88% yield. ^{1}H NMR (D_2O): δ 7.58−7.68 (m, 6 H, *H*6, *H*5), 8.03 (d, J = 8.4 Hz, 3 H, *H4*), 8.15 (d, J = 8.4 Hz, 3 H, *H2*). ^{31}P{^{1}H} NMR (D_2O): δ 44.00. ^{19}F NMR (D_2O): δ −115 (m, *o*-F), −158 (t, J = 10.7 Hz, *p*-F), −162 (m, *m*-F). Analysis calcd for $C_{24}H_{12}O_9F_5PS_3AuNa_3$·$H_2O$ (949.88) % C 30.32, H 1.49, S 10.10; found % C 29.99, H 1.55, S 10.51.

Preparation of [Au(C≡CR)(TPPTS)] Complexes. To a solution of the alkyne (0.32 mmol) and NaOH (0.014 g, 0.36 mmol) in MeOH (15 mL) was added solid [AuCl(TPPTS)] (0.2 mmol). After being stirred for ca. 15 h, the mixture was passed through Celite and the filtrate concentrated in vacuum to ca. 3 mL. Addition of Et_2O precipitated the product, which was isolated by filtration, washed with Et_2O, and dried. Some of the products consistently gave bad analyses even after repeated purification, presumably due to incomplete combustion.

[Au(C≡CR1)(TPPTS)] (R1 = C$_4$H$_9$). Pale yellow solid, 90% yield. ^{1}H NMR (D_2O): δ 0.78 (br. s, 3 H, CH_3), 1.27 (br. s, 4 H, CH_2), 2.10 (br. s, 2 H, CH_2C≡), 7.50−7.79 (m, 6 H, *H*6, *H*5), 7.79−8.10 (m, 6 H, *H*2, *H*4). ^{31}P{^{1}H} NMR (CD_3OD): δ 41.65. IR (KBr disk): 2124 cm^{-1} ν(C≡C). FAB-MS: 663 $[M]^+$, 767 $[M + Na]^+$. Analysis calcd for $C_{24}H_{21}O_9PS_3AuNa_3$·1.5NaCl (932.88) % C 30.87, H 2.27, S 10.28; found % C 30.47, H 1.98, S 10.15.

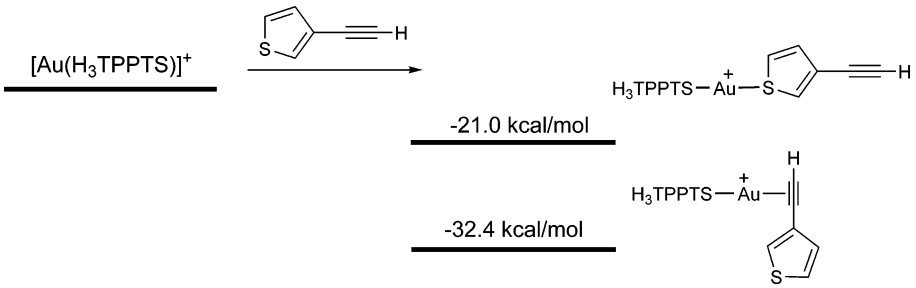

Figure 2. Computed relative stabilities of π-coordinated and *S*-coordinated isomers of $[Au(H_3TPPTS)(HC{\equiv}R3)]^+$ (R3 = 3-thiophenyl).

[Au(C≡CR2)(TPPTS)] (R2 = ^{t}Bu). Colorless solid, 90% yield. ^{1}H NMR (D_2O): δ 1.06 (s, 9 H, CH_3), 7.56−7.73 (m, 6 H, *H*6, *H*5), 7.80−8.04 (m, 6 H, *H*2, *H*4). $^{31}P\{^1H\}$ NMR (D_2O): δ 41.47. IR (KBr disk): 2101 cm^{-1} ν(C≡C). FAB-MS: 823 $[M - Na]^+$. Analysis calcd for $C_{24}H_{21}AuNa_3O_9PS_3$ (846.5) % C 34.37, H 2.35, S 11.16; found % C 34.05, H 2.50, S 11.36.

[Au(C≡CR3)(TPPTS)] (*R*3 = 3-Thiophenyl). Pale yellow solid, 65% yield. ^{1}H NMR (D_2O): δ 6.80 (d, J = 4.5 Hz, 1 H, thiophene-H_5), 7.17 (br. s, 1 H, thiophene-H_4), 7.23−7.31 (m, 1 H, thiophene-H_2), 7.53 (br. s, 3 H, *H*6), 7.68 (br. s, 3 H, *H*5), 7.76−7.99 (m, 6 H, *H*2, *H*4). $^{31}P\{^1H\}$ NMR (D_2O): δ 40.93. IR (KBr disk): 2107 cm^{-1} ν(C≡C). FAB-MS: 793 $[M - SO_3]^+$. Analysis calcd for $C_{24}H_{15}O_9PS_4AuNa_3{\cdot}2NaCl$ (987.79) % C 29.16, H 1.53, S 12.95; found % C 29.42, H 1.83, S 12.15.

[Au(C≡CR4)(TPPTS)] (R4 = 2-N-Me-Imidazolyl). Colorless solid, 53% yield. ^{1}H NMR (CD_3OD): δ 3.71 (s, 3 H, CH_3), 6.97 (s, 1 H, imidazole-H_3), 7.45−7.64 (m, 7 H, *H*6, *H*5, imidazole-H_5), 7.97 (d, J = 11.4 Hz, 3 H, *H*4), 8.09 (d, J = 11.4 Hz, 3 H, *H*2). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 29.59. IR (KBr disk): 2109 cm^{-1} ν(C≡C). FAB-MS: 871 $[M]^+$. Analysis calcd for $C_{24}H_{17}AuN_2Na_3O_9PS_3$ (870.50) % C 33.28, H 1.84, N 3.53, S 11.49; found % C 33.11, H 1.97, N 3.22, S 11.05.

[Au(C≡CR5)(TPPTS)] (R5 = 2-Pyridyl). Orange solid, 46% yield. ^{1}H NMR (CD_3OD): δ 7.11−7.29 (m, 1 H, Py-H_6), 7.29−7.48 (m, 1 H, Py-H_3), 7.48−7.97 (m, 9 H, *H*6, *H*5, *H*4), 7.97−8.28 (m, 4 H, *H*2, Py-H_4), 8.28−8.46 (m, 1 H, Py-H_6). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 42.55. IR (KBr disk): 2117 cm^{-1} ν(C≡C). FAB-MS: 868 $[M]^+$. Analysis calcd for $C_{25}H_{16}O_9NPS_3AuNa_3$ (876.50) % C 34.61, H 1.86, N 1.62, S 11.06; found % C 34.55, H 2.35, N 1.38, S 11.03.

[Au(C≡CR6)(TPPTS)] (R6 = 6-Methoxynaphthyl). Pale yellow solid, 45% yield. ^{1}H NMR (CD_3OD): δ 3.92 (s, 3 H, CH_3O), 7.08−7.15 (m, 1 H, Naph-H_5), 7.20 (s, 1 H, Naph-H_7), 7.42 (d, J = 8.3 Hz, 1 H, Naph-H_3), 7.52−7.78 (m, 9 H, *H*6, *H*5, *H*4), 7.80 (s, 1 H, Naph-H_4), 8.01−8.27 (m, 5 H, *H*2, Naph-H_1, Naph-H_8). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 42.28. IR (KBr disk): 2101 cm^{-1} ν(C≡C). FAB-MS: 969 $[M + Na]^+$. Analysis calcd for $C_{31}H_{21}AuNa_3O_{10}PS_3$ (946.60) % C 39.12, H 2.48, S 9.87; found % C 39.33, H 2.24, S 10.16.

[Au(C≡CR7)(TPPTS)] (R7 = Ferrocenyl). Orange solid, 77% yield. ^{1}H NMR (CD_3OD): δ 4.17 (m, 2 H, CpC≡C), 4.20 (m, 5 H, Cp), 4.36 (m, 2 H, CpC≡C), 7.55−7.75 (m, 9 H, *H*6, *H*5, *H*4), 8.03−8.18 (m, 3 H, *H*2). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 42.79. IR (KBr disk): 2103 cm^{-1} ν(C≡C). FAB-MS: 872 $[M - SO_3Na]^+$. Analysis calcd for $C_{30}H_{21}AuFeNa_3O_9PS_3$ (974.43) % C 37.11, H 2.30, S 9.53; found % C 36.98, H 2.17, S 9.87.

[Au(C≡CR8)(TPPTS)] (R8 = CH_2OH). Pale brown solid, 71% yield. ^{1}H NMR (CD_3OD): δ 4.24 (s, 2 H, CH_2), 7.51−7.71 (m, 9 H, *H*6, *H*5, *H*4), 7.99−8.18 (m, 3 H, *H*2). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 42.39. IR (KBr disk): 2127 cm^{-1} ν(C≡C). FAB-MS: 741 $[M - SO_3]^+$. Analysis calcd for $C_{21}H_{15}AuNa_3O_{10}PS_3$ (820.44) % C 30.37, H 1.56, S 11.35; found % C 30.74, H 1.84, S 11.72.

[Au(C≡CR9)(TPPTS)] (R9 = CMe_2OH). Colorless solid, 91% yield. ^{1}H NMR (CD_3OD): δ 1.27 (s, 6 H, CH_3), 7.43−7.74 (m, 6 H, *H*6, *H*5), 7.74−8.06 (m, 6 H, *H*4, *H*2). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 41.38. IR (KBr disk): 2123 cm^{-1} ν(C≡C). FAB-MS: 769 $[M - SO_3 + Na]^+$. Analysis calcd for $C_{23}H_{19}AuNa_3O_{10}PS_3$ (848.5) % C 32.16, H 2.75, S 11.12; found % C 32.56, H 2.26, S 11.34.

[Au(C≡CR10)(TPPTS)] (R10 = CPh_2OH). Colorless solid, 75% yield. ^{1}H NMR (CD_3OD): δ 7.03−7.23 (m, 6 H, Ph), 7.32−7.80 (m, 13 H, Ph, *H*6, *H*5, *H*4), 7.89 (d, J = 5.8 Hz, 3 H, *H*2). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 40.51. IR (KBr disk): 2112 cm^{-1} ν(C≡C). FAB-MS: 767 $[M-Na-CCPh_2OH]^+$. Analysis calcd for $C_{33}H_{23}AuNa_3O_{10}PS_3$ (972.63) % C 40.63, H 2.75, S 9.59; found % C 40.75, H 2.38, S 9.89.

[Au(C≡CR11)(TPPTS)] (R11 = CMeEtOH). Colorless solid, 91% yield. ^{1}H NMR (CD_3OD): δ 1.05 (t, J = 7.4 Hz, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.56−1.72 (m, 2 H, CH_2), 7.49−7.69 (m, 6 H, *H*6, *H*5), 7.95−8.14 (m, 6 H, *H*2, *H*4). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 41.10. IR (KBr disk): 2124 cm^{-1} ν(C≡C). FAB-MS: 635 $[M - Na]^+$, 619 $[M - Na - O]^+$, 1293 $[2M - Na]^+$, 1220 $[2M - (RC{\equiv}C)]^+$, 1095 $[2M - Au - Na - H]^+$. Analysis calcd for $C_{24}H_{23}AuNaO_4PS_3$ (658.43) % C 43.47, H 3.26, S 4.59; found % C 43.78, H 3.52, S 4.87.

[Au(C≡CR12)(TPPTS)] (R12 = 1-Hydroxycyclohexyl). Colorless solid, 93% yield. ^{1}H NMR (CD_3OD): δ 1.00−1.13 (m, 1 H, Cy), 1.21−1.44 (m, 2 H, Cy), 1.46−1.60 (m, 7 H, Cy), 7.46−7.70 (m, 6 H, *H*6, *H*5), 7.70−7.87 (m, 3 H, *H*4), 7.87−8.13 (m, 3 H, *H*2). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 41.15. IR (KBr disk): 2112 cm^{-1} ν(C≡C). FAB-MS: 707 $[M + Na]^+$, 1169 $[2M - 2(C_6H_{11}O) - H]^+$, 925 $[Au(TPPMS)_2]^+$, 561 $[Au(TPPMS)]^+$. Analysis calcd for $C_{26}H_{25}AuNaO_4PS_3$ (684.47) % C 45.23, H 3.57, S 4.12; found % C 45.62, H 3.68, S 4.68.

Alkyne Hydration Experiments. To mixture of MeOH (5 mL) and water (1 mL) were added the alkyne (0.5 mmol) followed by the gold catalyst and the acid in the amounts specified in Tables 1−4. The mixture was heated to reflux for 0.5, 1, or 1.5 h and then cooled to room temperature. The solution was passed through Celite and the filtrate analyzed by GC-MS.

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