Application of (phosphine)gold(I) carboxylates, sulfonates and related compounds as highly efficient catalysts for the hydration of alkynes

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Abstract

The catalytic activity of a series of six gold(I) complexes LAuX (L = Ph_3P, X = $CO_2C_2F_5$, SO_3-p-tol, SO_3Et, SSO_2-p-tol; L = Me_3P, (p-tol)$_3$P, X = $CO_2C_2F_5$), as well as the silver(I) complexes $Ph_3PAgOC(O)C_2F_5$ and $Ph_3PAgOS(O)_2$-p-tol·EtOH, regarding the hydration of 3-hexyne forming 3-hexanone in the presence of BF_3·Et_2O as a co-catalyst has been investigated. It could be shown that all the gold compounds are catalytically active with (Ph_3P)AuOC(O)C_2F_5 (**1**) being the most active. Using **1**, hydration of 3-hexyne takes place at room temperature and turnover frequencies (TOFs) as high as $3900\,h^{-1}$ can be reached without any notable catalyst deterioration (MeOH as solvent, $70\,°C$). The silver complexes on the other hand did not furnish 3-hexanone under reaction conditions. This observation is explained with silver being the stronger acceptor compared to gold which can be derived from the crystal structures of representative examples. An optimization of the co-catalyst concentration showed that with increasing concentration the reaction rate increases significantly reaching saturation at approximately 5 mol%. This indicates that the Lewis acid BF_3·Et_2O plays a role in several steps of the catalytic cycle. **1** was also successfully employed as a catalyst to react acetic acid with 3-hexyne forming 3-hexene-3-acetate but due to water being present in the glacial acetic acid 3-hexanone was also formed.
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1. Introduction

One of the most straightforward ways to generate compounds with carbon–oxygen bonds is the hydration of unsaturated organic compounds. An efficient hydration process is not only environmentally benign but also economically attractive. Especially the synthesis of carbonyl compounds by addition of water to alkynes has been extensively studied [1]. It has long been known that water can be added quite easily to activated electron-rich alkynes such as alkynylethers or alkynylthioethers in the presence of an acid catalyst [2]. However, simple alkynes are not readily hydrated even in the presence of a co-catalyst (typically toxic mercury(II) salts) [3]. Several transition metal catalysts containing $Ru^{II,III}$ [4], Rh^{I} [5], Pt^{II} [6], Au^{III} [7] and other metals [8] have also been employed in the past, but only with limited success. The best results were obtained for the hydration of 3-pentyn-1-ol in the presence

of [cis-PtCl$_2$(tpps)$_2$] (tpps = P(m-$C_6H_4SO_3Na$)$_3$) with an initial turnover frequency (TOF) of $550\,h^{-1}$ and an overall TOF of not more than approximately $100\,h^{-1}$ [6c].

In 1998, Teles et al. have shown that certain (phosphine)gold(I) complexes of the type (R_3P)Au$^+X^-$ are extremely efficient catalysts for the addition of methanol to alkynes in the presence of Brønsted or Lewis acidic co-catalysts [9a]. In their patent application [9b], the authors also briefly mentioned the addition of water to propargyl alcohol, but quoted only low yields.

These new results have been an incentive for extensive research in gold catalysis [10], a topic which had been neglected for a long time, as gold was often thought of as "catalytically dead" [11]. Very recently, Tanaka and co-workers found (triphenylphosphine)gold(I) sulfate to be a very active catalytic system for the hydration of 1-octyne. Conversion into 2-octanone proceeds in high yields and with turnover frequencies of approximately $3500\,h^{-1}$. Since the catalyst deteriorates under the standard reaction conditions ($70\,°C$; MeOH as solvent), the addition of additives such as carbon monoxide is necessary to stabilize the system. With this precaution higher yields and reaction rates

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(TOF $= 15{,}600\,h^{-1}$) have been achieved [12]. In the light of this encouraging progress, we initiated a search for a catalyst which is stable under standard reaction conditions which could serve in an environmentally and economically benign process without gaseous additives. In the present report it is demonstrated that (phosphine)gold(I) carboxylates and (phosphine)gold(I) sulfonates are highly active and reusable catalysts for the addition of water to non-activated alkynes. The addition of acetic acid to those substrates was also successful.

2. Experiments

2.1. Materials

Syntheses of the catalysts were carried out in an atmosphere of dry nitrogen. Glassware was oven-dried, evacuated and flushed with nitrogen. Solvents were dried, distilled and stored under a nitrogen atmosphere. Standard equipment was used throughout. The glass apparatus was protected against light by an aluminum foil wrapper. Silver pentafluoropropionate and all tertiary phosphines are commercially available. (Phosphine)gold(I) chlorides [13] and silver sulfonates [14] were prepared according to literature procedures. The synthesis as well as structural and spectroscopic data for the catalysts used has recently been published elsewhere [15]. Therefore, only four representative examples are described in detail here.

2.2. Synthesis of (triphenylphosphine)gold(I) pentafluoropropionate (1)

A solution of (Ph₃P)AuCl (300 mg, 0.60 mmol) in dichloromethane (10 ml) was added to a suspension of F₅C₂COOAg (200 mg, 0.74 mmol) in the same volume of the same solvent at $-78\,^{\circ}$C with stirring and under protection against incandescent light. The mixture was stirred for 3 h and subsequently filtered. The product was precipitated from the filtrate by addition of pentane, collected by filtration and recrystallized from dichloromethane (320 mg, 85% yield), mp 134 $^{\circ}$C (decomposition). NMR (CD₂Cl₂, 20 $^{\circ}$C), ^{1}H: 6.68–7.12, m, Ph. ^{13}C{^{1}H}: 128.4, d, $J = 67.7$ Hz, C (*ipso*); 129.8, d, $J = 12.3$ Hz, C (*meta*); 132.7, d, $J = 2.3$ Hz, C (*para*); 134.6, d, $J = 13.1$ Hz, C (*ortho*). ^{19}F{^{1}H}: -6.3, t, $^{3}J_{FF} = 112$ Hz, CF₃; -42.7, q, $^{3}J_{FF} = 112$ Hz, CF₂. ^{31}P{^{1}H}: 27.5, s. MS (FAB): m/z 1081, 10% [(Ph₃PAu)₂OCOC₂F₅]$^{+}$; 721, 18% [(Ph₃P)₂Au]$^{+}$; 459, 100% [Ph₃PAu]$^{+}$. C₂₁H₁₅AuO₂PF₅ (619.27) calcd. C 40.5, H 2.4; found C 40.8, H 2.5.

2.3. Synthesis of (triphenylphosphine) gold(I)-p-tolylsulfonate (4)

A suspension of silver *p*-tolylsulfonate (300 mg, 1.1 mmol) in dichloromethane (20 ml) was treated with a solution of Ph₃PAuCl (500 mg, 1.0 mmol) in CH₂Cl₂

(10 ml) at 20 $^{\circ}$C for 3 h with stirring. The AgCl precipitate was filtered off and the product precipitated from the clear filtrate by addition of pentane. The product was filtered, washed with toluene and crystallized from CH₂Cl₂/pentane at $-30\,^{\circ}$C; colorless rods containing dichloromethane, 490 mg (78% yield), mp 162 $^{\circ}$C with decomposition. NMR (CDCl₃, 20 $^{\circ}$C), ^{1}H: 7.9–7.1, m, 19H, C₆H₅/C₆H₄; 2.41, s, 3H, Me; 5.3, s, 2H, CH₂Cl₂. ^{31}P{^{1}H}: 27.9, s. ^{13}C{^{1}H}: 134.1, d, $J = 14.0$ Hz; 132.2, s; 129.3, d, $J = 12.3$ Hz; 127.6, d, $J = 64.9$ Hz for $o, p, m, ipso$ in C₆H₅; 141.7, 139.2, 129.0, and 126.5, all s for *ipso*, *o*, *m*, and *p* in C₆H₄; 53.3, s for CH₂Cl₂, 21.3, s for Me. IR (KBr): 1261, 1184, 1146, 1100, 954 cm^{-1} (ν(SO₃R)). MS (FAB): m/z 721, 11% [(Ph₃P)₂Au]$^{+}$; 631, 3% [$M+1$]$^{+}$; 459, 100% [(Ph₃P)Au]$^{+}$; 262, 6% [Ph₃P]$^{+}$. C₂₆H₂₄AuCl₂O₃PS (715.35) calcd. C 43.6, H 3.4, S 4.5; found C 44.1, H 3.3, S 4.4.

2.4. Synthesis of (triphenylphosphine)silver(I) pentafluoropropionate (7)

A suspension of C₂F₅CO₂Ag (250 mg, 0.93 mmol) in 10 ml of dichloromethane was treated with a solution of Ph₃P (240 mg, 0.93 mmol) in the same volume of the same solvent at room temperature. A clear solution was obtained, the volume of which was reduced to ca. 5 ml in a vacuum. Addition of cold pentane ($-70\,^{\circ}$C) gave a colorless precipitate which was recrystallized from dichloromethane/pentane, yield 450 mg (91%), mp 208 $^{\circ}$C. NMR (CDCl₃, 20 $^{\circ}$C), ^{1}H: 7.38–7.56, m, Ph. ^{13}C{^{1}H}: 163.2, t, J 25.5 Hz, CO₂; CF₂ and CF₃ were not detected; 128.9, d, $J = 37.4$ Hz; 129.3, d, $J = 10.1$ Hz; 131.5, s; 133.9, d, $J = 17.0$ Hz (for C *ipso*, *meta*, *para*, and *ortho*, respectively). ^{31}P{^{1}H}: 15.4, s. IR (KBr): 1653 cm^{-1} (ν(CO)). MS (FAB): m/z 631, 31.1% [L₂Ag]$^{+}$; 385, 3.0% [LAgO]$^{+}$; 369, 100% [LAg]$^{+}$; 262, 47.5% [L]$^{+}$. C₂₁H₁₅AgO₂PF₅ (533.17) calcd. C 47.3, H 2.8, P 5.8; found C 47.3, H 2.7, P 6.2.

2.5. Synthesis of (triphenylphosphine) silver(I)-p-tolylsulfonate (ethanol) (8)

4-MeC₆H₄SO₃Ag (290 mg, 1.04 mmol) was suspended in a mixture of dichloromethane and ethanol (10 ml each) at room temperature and treated with Ph₃P (270 mg, 1.04 mmol) for 2 h with stirring to give an almost clear colorless solution. Small amounts of residue were filtered off and the volume of the filtrate was reduced to a few ml. The product was precipitated by addition of pentane, filtered, washed with pentane and diethylether, and dried in a vacuum, yield 430 mg (76%), mp 124 $^{\circ}$C (with decomposition). Single crystals can be grown from pentane/ethanol at $-30\,^{\circ}$C. NMR (CDCl₃, 20 $^{\circ}$C), ^{1}H: 6.87–7.96, m, 19H, Ph and C₆H₄; 3.55, q, 2H, $J = 7.4$ Hz, CH₂; 2.14, s, 3H, 4-Me; 1.16, t, 3H, Me. ^{31}P{^{1}H}: 14.2, s. MS (FAB): m/z 910, 5.4% [(Ph₃P)₂Ag₂SO₃C₆H₄Me]$^{+}$; 631, 16.3% [(Ph₃P)₂Ag]$^{+}$; 369, 100% [Ph₃PAg]$^{+}$; 262, 26.4% [Ph₃P]$^{+}$.

$C_{27}H_{28}AgO_4PS$ (587.40) calcd. C 55.2, H 4.8, S 5.5; found C 55.4, H 4.6, S 5.7.

2.6. Addition of water to 3-hexyne

In a typical procedure, a solution of 3-hexyne (1.00 g, 12.05 mmol) in 5 ml of THF (or MeOH) was mixed with water (870 mg, 48.2 mmol, 4 equiv.) and $BF_3 \cdot Et_2O$ (90 mg, 5.25 mol%). The mixture was heated to the reaction temperature and the reaction was started by adding a gold catalyst, for example, $Ph_3PAuOC(O)C_2F_5$ (**1**, 10 mg, 0.016 mol, 0.134 mol%). At regular intervals, small samples were taken and analyzed by gas chromatography.

2.7. Addition of water to phenylacetylene

One gram of phenylacetylene (9.79 mmol) was dissolved in THF (5 ml) and treated with water (720 mg, 39.16 mmol, 4 equiv.) in a small flask. After heating the reaction mixture to 45 °C in a water bath $BF_3 \cdot Et_2O$ (73 mg, 5.25 mol%) and (triphenylphosphine)gold(I)-p-tolylsulfonate (8.3 mg, 0.132 mol%) were added to start the catalysis. The reaction mixture was analyzed in regular intervals using gas chromatography.

2.8. Addition of water to cyclopentylacetylene

Five hundred milligrams of cyclopentylacetylene (4.60 mmol) were dissolved in THF (5 ml) and treated with water (340 mg, 18.80 mmol, 4 equiv.) in a small flask. After heating the reaction mixture to 45 °C in a water bath, $BF_3 \cdot Et_2O$ (34 mg, 5.25 mol%) and (triphenylphosphine)gold (I)-p-tolylsulfonate (4.0 mg, 0.132 mol%) were added to start the reaction. The mixture was analyzed in regular intervals using gas chromatography.

2.9. Addition of acetic acid to 3-hexyne

A small flask was charged with 3-hexyne (1.00 g, 12.05 mmol), THF (5 ml), glacial acetic acid (3.61 g, 5 eqiv.) and $BF_3 \cdot Et_2O$ (90 mg, 5.25 mol%). The mixture was heated to 60 °C and the reaction was started by adding (triphenylphosphine)gold(I) pentafluoropropionate (10 mg, 0.016 mmol, 0.134 mol%). After a reaction time of 1 h, an excess of cold (−60 °C) pentane was added in order to precipitate the gold catalyst and to stop the reaction. After filtration, the mixture was analyzed using gas chromatography.

3. Results and discussion

In preliminary experiments, the complexes $Ph_3PAuOC(O)C_2F_5$ (**1**), $(p\text{-tol})_3PAuOC(O)C_2F_5$ (**2**), $Me_3PAuOC(O)C_2F_5$ (**3**), $Ph_3PAuOS(O)_2\text{-}p\text{-tol}$ (**4**), $Ph_3PAuOS(O)_2Et$ (**5**), $Ph_3PAuSS(O)_2\text{-}p\text{-tol}$ (**6**), $Ph_3PAgOC(O)C_2F_5$ (**7**), and $Ph_3PAgOS(O)_2\text{-}p\text{-tol}\cdot EtOH$ (**8**) were chosen for a study of their catalytic properties and applied to the reaction of water with 3-hexyne in THF in the presence of $BF_3 \cdot Et_2O$ as a co-catalyst at 45 °C (Scheme 1). The structural and spectroscopic data for complexes **1**–**8** have recently been discussed elsewhere [15].

The results of the catalysis experiments are summarized in Table 1. It appears that the nature of the anions is a very important factor with respect to the catalytic activity, as already observed by Teles et al. for the addition of alcohols to alkynes in the presence of gold(I) catalysts [9]. The activity of the compounds is strongly related to the "hardness" of the anions, since the LAu^+ cation (L = ligand) is likely to be the catalytically active species [9a]. This cation coordinates to the alkyne in the first step of the catalytic cycle, thus rendering it more susceptible for a nucleophilic attack. Therefore, it is not surprising that $(Ph_3P)AuSS(O)_2\text{-}p\text{-tol}$ (**6**) containing the softer p-tolylthiosulfonate anion furnishes only traces of 3-hexanone after 48 h, whereas $(Ph_3P)AuOS(O)_2\text{-}p\text{-tol}$ (**4**) containing the harder p-tolylsulfonate anion yields more than 80% of the ketone product after only 4 h of reaction time (TOF = $155 \, h^{-1}$). Even better results were obtained using $(Ph_3P)AuOS(O)_2Et$ (**5**) which leads to a TOF of $160 \, h^{-1}$. The most active compound however turned out to be $(Ph_3P)AuOC(O)C_2F_5$ (**1**) containing the extremely hard pentafluoropropionate anion, giving rise to a turnover frequency of $213 \, h^{-1}$.

As far as the phosphine ligands are concerned, the activity increases as poor phosphinedonors are employed. Therefore, compound **1** containing triphenylphosphine is more active than compounds **2** (TOF = $163 \, h^{-1}$) and **3** (TOF = $99 \, h^{-1}$) containing the more strongly donating ligands tri-p-tolylphosphine and trimethylphosphine, respectively. Even better results are therefore to be expected using very electron-poor donors such as triphenylphosphite $(PhO)_3P$, but their complexes with sulfonate or carboxylate counterions are not stable under the reaction conditions and therefore catalyst deterioration occurs very quickly. These observations again resemble the results obtained by Teles et al. for the addition of alcohols to alkynes using gold(I) sulfate complexes and sulfuric acid as the catalytic system [9a].
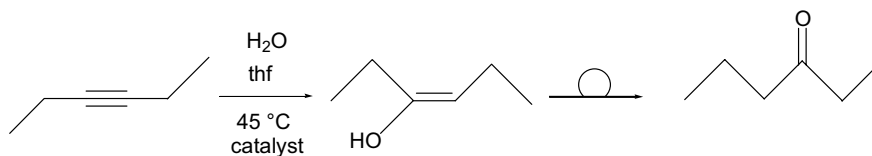
Scheme 1. Catalytic hydration of 3-hexyne.

Table 1
Hydration of 3-hexyne in the presence of various catalysts[a]

Catalyst	mol% Catalyst referred to 3-hexyne	Time (h)	Yield (%)[b]	TOF (h^{-1})
(Ph$_3$P)AuOC(O)C$_2$F$_5$ (**1**)	0.134	1.8	51.2	213
[(p-Tol)$_3$P]AuOC(O)C$_2$F$_5$ (**2**)	0.137	2	43.2	163
(Me$_3$P)AuOC(O)C$_2$F$_5$ (**3**)	0.095	2	18.8[c]	99[c]
(Ph$_3$P)AuOS(O)$_2$-p-tol (**4**)	0.132	4	82.1	155
(Ph$_3$P)AuOS(O)$_2$Et (**5**)	0.146	1.5	35.0	160
(Ph$_3$P)AuSS(O)$_2$-p-tol (**6**)	0.129	48	0.12	0.02
(Ph$_3$P)AgOC(O)C$_2$F$_5$ (**7**)	0.156	48	–	–
(Ph$_3$P)AgOS(O)$_2$-p-tol·EtOH (**8**)	0.167	48	–	–

[a] Reaction conditions: 1.0 g of 3-hexyne (12.05 mmol); 870 mg of H$_2$O (4 eqiv.); 5.25 mol% BF$_3$·Et$_2$O; 5 ml of THF; 45 °C.

[b] Determined using gas chromatography (diethyleneglycol-di-n-butylether as the internal standard).

[c] After a few minutes decomposition to elemental gold occurred.

Under the same reaction conditions as applied for analogous gold compounds the silver complexes (Ph$_3$P)AgOC(O)C$_2$F$_5$ (**7**) and (Ph$_3$P)AgOS(O)$_2$-p-tol (**8**) showed no catalytic activity. An explanation for this phenomena can be based on the comparison of the crystal structures of compounds **4** and **8** (Fig. 1) which have already been published [15a,c]. The mode of dimerization found in (Ph$_3$P)AgOS(O)$_2$-p-tol (**8**) reflects the high acceptor character of the silver atoms in these sulfonate complexes which leads not only to strong binding of an extra oxygen atom of a neighboring molecule but also to a fixation of an ethanol solvent molecule [15c]. For the corresponding gold complexes, no such acceptor properties are discernible. In crystals of (Ph$_3$P)AuOS(O)$_2$-p-tol (**4**), the monomers are only weakly associated via aurophilic contacts and no solvent is accepted in the coordination sphere of the metal atoms [15a].
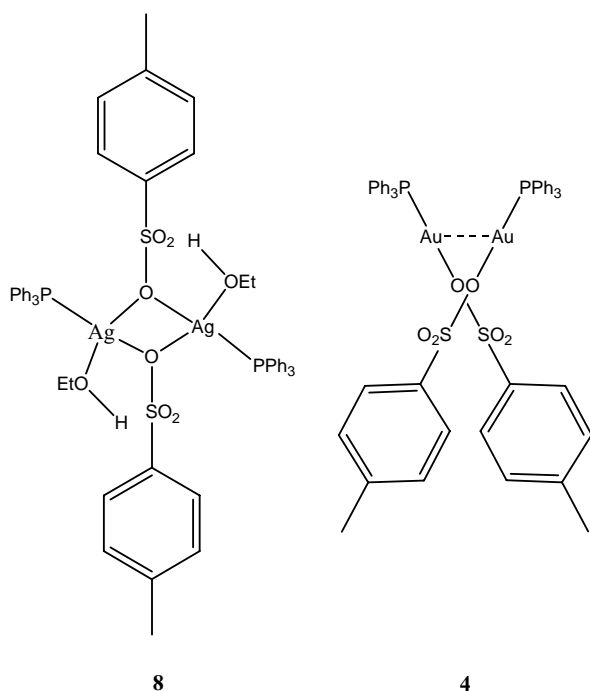
The low catalytic reactivity of LAgX as compared to LAuX complexes, e.g. in the addition of nucleophiles to alkynes, is readily explained by the much stronger ligand binding at the silver atoms. The proposed active [LAg]$^+$ species are therefore much less abundant in the corresponding dissociation equilibria than the [LAu]$^+$ species [15a,c,16]. High [LAg]$^+$ activity is to be expected only in cases with counterions X$^-$ devoid of any donor capacity and in the complete absence of donor solvent molecules. The corresponding gold systems are much less sensitive to the nature of X$^-$ and of the solvent owing to the strongly reduced acceptor properties of the metal atom.

As (Ph$_3$P)AuOC(O)C$_2$F$_5$ (**1**) turned out to be the most active catalyst among the complexes investigated, this compound was subsequently used for an investigation of the influence of the reaction temperature on the activity. The reaction of 3-hexyne with water in the presence of BF$_3$·Et$_2$O was again used as a model system. Since the results of Tanaka and co-workers indicated that the reaction rate in their catalytic system improves significantly by using methanol instead of THF as a solvent [12], experiments with both solvents were carried out at different temperatures. The results of these investigations are given in Table 2.

The results indicate that (Ph$_3$P)AuOC(O)C$_2$F$_5$ (**1**) is a very active catalyst for hydration reactions of non-activated

Fig. 1. Comparison of the structural motifs found in complexes (Ph$_3$P)AuOS(O)$_2$-p-tol (**4**) and (Ph$_3$P)AgOS(O)$_2$-p-tol (**8**).

Table 2
Temperature and solvent dependence of the hydration of 3-hexyne catalyzed by (Ph$_3$P)AuOC(O)C$_2$F$_5$ (**1**)[a]

Entry	Temperature (°C)	Solvent (5 ml)	Time (h)	Yield (%)[b]	TOF (h^{-1})
1	22	THF	2	13.9	28
2	30	THF	2	34.7	70
3	45	THF	1.8	51.2	213
4	45	MeOH	0.8	86.8	790
5	60	THF	1	56.6	424
6	60	MeOH	0.2	55.5	2078
7	70	MeOH	0.1	52.1	3900

[a] Reaction conditions: 1.0 g of 3-hexyne (12.05 mmol); 870 mg of H$_2$O (4 eqiv.); 5.25 mol% BF$_3$·Et$_2$O; 10 of mg (Ph$_3$P)AuOC(O)C$_2$F$_5$ (**1**, 0.134 mol%).

[b] Determined using gas chromatography (diethyleneglycol-di-n-butylether as the internal standard).
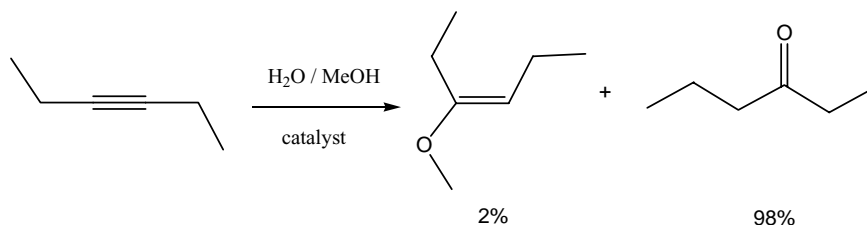
Scheme 2. Products of the hydration of 3-hexyne in aqueous methanol as solvent.

alkynes. The reaction takes place even at room temperature (Table 2, entry 1). It is not surprising that the activity increases significantly with increasing reaction temperatures, and for THF as a solvent the activity rises from $28\,h^{-1}$ at room temperature up to $424\,h^{-1}$ at $60\,°C$. As already presumed, even higher reaction rates are observed using methanol instead of THF as a solvent. Thus, the TOF can be raised up to $3900\,h^{-1}$ at $70\,°C$ without any detectable catalyst deterioration. The catalyst can be recycled and reused. Even after five catalytic cycles, the activity stays the same within the precision range of the measurements. The turnover number after five cycles was approximately 3400, but it should be possible to increase this value even further. However, using methanol as a solvent gives rise to the formation of a small amount of 3-methoxy-3-hexene as a byproduct due to the addition of methanol to the triple bond (Scheme 2).

In another set of experiments, the addition of water (870 mg, 4 eqiv.) to 3-hexyne (1.00 g, 12.05 mmol) in THF (5 ml) at $45\,°C$ in the presence of (triphenylphosphine)gold (I)-*p*-tolylsulfonate (**4**, 10 mg, 0.132 mol%) as the catalyst was optimized in respect of the co-catalyst (BF$_3$·Et$_2$O) concentration. The results are summarized in Table 3. It is interesting to note that neither without catalyst nor without co-catalyst any reaction is observed.

Moreover, it appears that with increasing co-catalyst concentration the reaction rate increases significantly reaching saturation at approximately 5 mol% (referring to 3-hexyne; Table 3, entry 7). Using even higher concentrations of BF$_3$·Et$_2$O does not lead to a further increase of the reaction rate. A visualization of these results is given in Fig. 2.

Table 4
Influence of the substrate on the reaction rate and the regioselectivity

Substrate	Time (h)	Yield (%)	TOF (h^{-1})	Markovnikov addition (%)
3-Hexyne	4	82.1	155	–
Phenylacetylene	4	6.4	12.0	98.8
Cyclopentylacetylene	4	7.1	13.6	99.6

These results indicate that the co-catalyst is not only needed to remove the counterions of the gold complexes, thus forming the catalytically active cationic species, but should also play an important role in other steps of the catalytic cycle of the reaction. In the mechanism proposed by Teles et al. [9a], it has been proposed that organogold intermediates **E** and **F** are formed during the addition of methanol to propyne (Scheme 3), and it is likely that the addition of water to an alkyne should proceed similarly. As BF$_3$·Et$_2$O forms HF upon hydrolysis under the reaction conditions, it is likely that the hydrofluoric acid produced in this process also accelerates the cleavage of the gold–carbon bonds of the reaction intermediates.

The regioselectivity and the influence of the substrate on the reaction rate were investigated using unsymmetrically substituted alkynes. Phenylacetylene and cyclopentylacetylene were reacted with water (4 eqiv.) under the same conditions as described above ($45\,°C$, 5.25 mol% BF$_3$·Et$_2$O, 5 ml of THF) using (triphenylphosphine)gold(I)-*p*-tolylsulfonate (**4**, 0.132 mol%) as a catalyst. The results show that in both cases Markovnikov addition is strongly favored (Table 4). It also appears that the substrate has a great influence on the

Table 3
Influence of the co-catalyst concentration on the reaction rate[a]

Entry	Co-catalyst		Time (h)	Yield (%)[b]	TOF (h^{-1})
	mg	mol%			
1 (Without catalyst)	90 (BF$_3$·Et$_2$O)	5.25	24	–	–
2	–	–	24	–	–
3	7 (BF$_3$·Et$_2$O)	0.41	2	0.1	0.38
4	15 (BF$_3$·Et$_2$O)	0.88	2	0.3	1.1
5	30 (BF$_3$·Et$_2$O)	1.75	2	18.7	70.8
6	45 (BF$_3$·Et$_2$O)	2.6	2	27	102
7	90 (BF$_3$·Et$_2$O)	5.25	2	42	159
8	180 (BF$_3$·Et$_2$O)	10.5	2	42.4	160

[a] Reaction conditions: 1.0 g of 3-hexyne (12.05 mmol); 870 mg of H$_2$O (4 eqiv.); 10 mg of (Ph$_3$P)AuOS(O)$_2$-*p*-tol (**4**, 0.132 mol%); 5 ml of THF; $45\,°C$.
[b] Determined using gas chromatography (diethyleneglycol-di-*n*-butylether as internal standard).
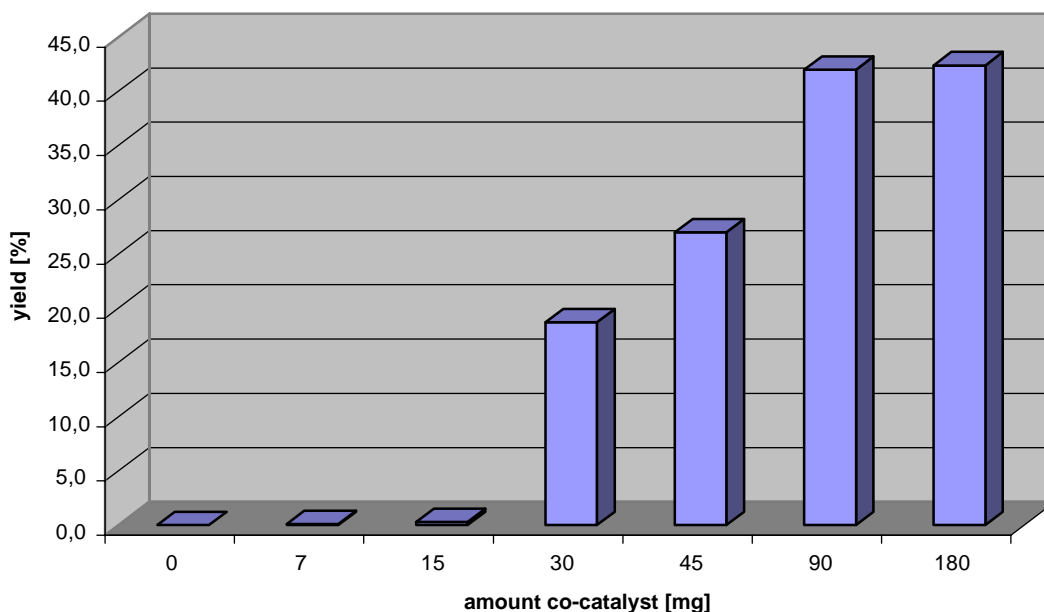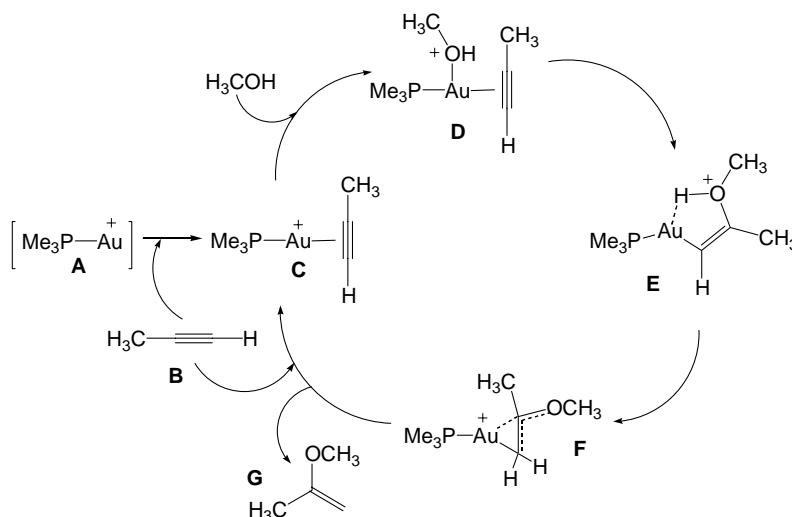
Fig. 2. Influence of the co-catalyst concentration on the reaction rate.

Scheme 3. Proposed mechanism for the addition of MeOH to propyne [9a].

reaction rates. Phenylacetylene and cyclopentylacetylene react more than one order of magnitude slower as compared to 3-hexyne.

Using (triphenylphosphine)gold(I) pentafluoropropionate (**1**, 10 mg, 0.016 mmol, 0.134 mol%) as a catalyst it was possible to add acetic acid (3.61 g, 5 eqiv.) to 3-hexyne (1.00 g, 12.05 mmol). The reaction of glacial acetic acid with 3-hexyne was carried out at 60 °C in 5 ml of THF and in the presence of $BF_3 \cdot Et_2O$ as a co-catalyst (5.25 mol%). After 1 h reaction time, both 3-hexanone (yield 12.3%) and 3-hexene-3-acetate (yield 6.2%) could be detected using gas chromatography. Not surprisingly water present in small amounts in glacial acetic acid reacts preferentially due to its stronger nucleophilic character as compared to acetic acid. Addition of two molecules of acetic acid to the triple

bond was not observed. If the same quantities of acetic acid, 3-hexyne and $BF_3 \cdot Et_2O$ are mixed and heated to 60 °C without adding a gold catalyst no reaction occurs at all.

4. Conclusion

It could be shown that (phosphine)gold(I) carboxylates and sulfonates are highly active catalysts for hydration reactions of non-activated alkynes. Analogous silver(I) complexes are not active in this respect due to the fact that silver(I) cations are much stronger acceptors for their ligands and counterions as compared to gold(I) cations. (Triphenylphosphine)gold(I) pentafluoropropionate (**1**), the most active of the compounds investigated catalyzes the addition

of water to 3-hexyne even at room temperature. The complex **1** can also be used at 70 °C. Under these conditions, turnover frequencies as high as 3900 h^{-1} are reached without the need for protective gaseous additives such as carbon monoxide to prevent catalyst deterioration. The catalyst was successfully recycled and reused five times without any notable loss of activity.

For the reaction of 3-hexyne with water, the co-catalyst concentration was optimized. The results indicate that the co-catalyst serves more than one purpose in the catalytic cycle. Again, using **1** as a catalyst, it was possible to add acetic acid to 3-hexyne to give 3-hexene-3-acetate. With water present in glacial acetic acid, 3-hexanone is also formed.

The results call for further investigations in order to finally reach a level which is acceptable as an environmentally as well as economically benign process for industrial applications.

Acknowledgements

References

[1] (a) P.F. Hudrlik, A.M. Hudrlik, in: S. Patai (Ed.), The Chemistry of the Carbon–Carbon Triple Bond. Part 1, Wiley, New York, 1978, p. 199;
(b) G.H. Schmid, in: S. Patai (Ed.), The Chemistry of the Carbon–Carbon Triple Bond. Part 1, Wiley, New York, 1978, p. 275;
(c) J. March, Advanced Organic Chemistry, Wiley, New York, 1992, p. 762;
(d) A. Schrohe, Chem. Ber. 8 (1875) 367;
(e) A. Bayer, Chem. Ber. 15 (1882) 2705;
(f) W.H. Perkin Jr., J. Chem. Soc. 45 (1884) 170;
(g) T. Tsuchimoto, T. Joya, E. Shirakawa, Y. Kawakami, Synlett 12 (2000) 1777;
(h) Y. Izumi, Catal. Today 33 (1997) 371;
(i) I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[2] (a) W. Drenth, H. Hogeveen, Recl. Trav. Chim. Pays-Bas 79 (1960) 1002;
(b) A.D. Allen, Y. Chiang, A.J. Kresge, T.T. Tidwell, J. Org. Chem. 47 (1982) 775, and references therein.
[3] (a) V. Jäger, H.G. Viehe, Methoden d. Organic Chemistry, vol. 5/2a, 4th ed., Houben-Weyl, 1977, p. 726;
(b) M. Kutscheroff, Chem. Ber. 17 (1884) 13;
(c) R.J. Thomas, K.N. Campbell, G.F. Hennion, J. Am. Chem. Soc. 60 (1938) 718;
(d) J.S. Reichert, J.H. Bailey, J.A. Niewland, J. Am. Chem. Soc. 45 (1923) 1553;
(e) H.D. Hinton, J.A. Niewland, J. Am. Chem. Soc. 52 (1930) 1553;
(f) D.B. Killian, G.F. Hennion, J.A. Niewland, J. Am. Chem. Soc. 56 (1934) 1384;
(g) M. Basetti, B. Floris, J. Chem. Soc., Perkin Trans. II (1988) 227.
[4] (a) M. Tokunaga, Y. Wakatsuki, Angew. Chem. Int. Ed. 37 (1998) 2867;
(b) T. Suzuki, M. Tokunaga, Y. Wakatsuki, Org. Lett. 3 (2001) 735;
(c) M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi, Y. Wakatsuki, J. Am. Chem. Soc. 123 (2001) 11917;
(d) D.B. Grotjahn, C.D. Incarvito, A.L. Rheingold, Angew. Chem. Int. Ed. 40 (2001) 3884;
(e) J. Harpern, B.R. James, A.L.W. Kemp, J. Am. Chem. Soc. 83 (1961) 4097;
(f) J. Harpern, B.R. James, A.L.W. Kemp, J. Am. Chem. Soc. 88 (1966) 5142;
(g) T. Khan, S.B. Halligudi, S. Shukla, J. Mol. Catal. 58 (1990) 299.
[5] (a) B.R. James, G.L. Rempel, J. Am. Chem. Soc. 91 (1969) 863;
(b) J. Blum, H. Huminer, H. Alper, J. Mol. Catal. 75 (1992) 153.
[6] (a) W. Hiscox, P.W. Jennings, Organometallics 9 (1990) 1997;
(b) W. Baidossi, M. Lahav, J. Blum, J. Org. Chem. 62 (1997) 669;
(c) L.W. Francisco, D.A. Moreno, J.D. Atwood, Organometallics 20 (2001) 4237.
[7] (a) Y. Kukuda, K. Utimoto, J. Org. Chem. 56 (1991) 3729;
(b) Y. Fukuda, K. Utimoto, Bull. Chem. Soc. Jpn. 64 (1991) 2013.
[8] (a) K. Imi, K. Imai, K. Utimoto, Tetrahedron Lett. 28 (1987) 3127;
(b) I.K. Meier, J.A. Marsella, J. Mol. Catal. 78 (1993) 31.
[9] (a) J.H. Teles, S. Brode, M. Chabanas, Angew. Chem. Int. Ed. 37 (1998) 1415;
(b) J.H. Teles, M. Schulz, WO-A1 9721648 (1997), to BASF AG.
[10] (a) R.O.C. Norman, W.J.E. Parr, C.B. Thomas, J. Chem. Soc., Perkin Trans. I (1976) 1983;
(b) D. Thompson, Gold Bull. 31 (1998) 111;
(c) D. Thompson, Gold Bull. 32 (1999) 12;
(d) G.C. Bond, D.T. Thompson, Catal. Rev. 41 (1999) 319;
(e) G.C. Bond, Gold Bull. 34 (2001) 117;
(f) G. Dyker, Angew. Chem. Int. Ed. 39 (2000) 4237;
(g) G.J. Hutchings, Catal. Today 72 (2002) 11;
(h) A.S.K. Hashmi, Gold Bull. 36 (2003) 3;
(i) Y. Ito, M. Sawamura, T. Hayashi, J. Am. Chem. Soc. 108 (1986) 6405;
(j) S. Komiya, T. Sone, Y. Usui, M. Hirano, A. Fukuoda, Gold Bull. 29 (1996) 131;
(k) V.A. Soloshonok, T. Hayashi, Tetrahedron Asymmetry 6 (1994) 1091;
(l) J.E. Parkes, A.I. Balch, J. Organomet. Chem. 71 (1974) 453;
(m) A.S.K. Hashmi, T.M. Frost, J.W. Bats, Catal. Today 72 (2002) 19;
(n) A.S.K. Hashmi, T.M. Frost, J.W. Bats, Org. Lett. 3 (2001) 3769;
(o) N. Asao, K. Takahashi, S. Lee, T. Kasahara, Y. Yamamoto, J. Am. Chem. Soc. 124 (2002) 12650;
(p) A.S.K. Hashmi, T.M. Frost, J.W. Bats, J. Am. Chem. Soc. 122 (2000) 11553;
(q) A. Hoffmann-Röder, N. Krause, Org. Lett. 3 (2001) 2537;
(r) A.S.K. Hashmi, L. Schwarz, J.H. Choi, T.M. Frost, Angew. Chem. Int. Ed. 39 (2000) 2285;
(s) J. Dankwardt, Tetrahedron Lett. 42 (2001) 5809;
(t) Y. Fukuda, K. Utimoto, H. Nozaki, Heterocycles 25 (1987) 297;
(u) T.E. Müller, M. Beller, Chem. Rev. 98 (1998) 675;
(v) R. Lok, R.E. Leone, A.J. Williams, J. Org. Chem. 61 (1996) 3289;
(w) A.S.K. Hashmi, L. Ding, J.W. Bats, P. Fischer, W. Frey, Chem. Eur. J. 9 (2003) 4339;
(x) G.J. Hutchings, R. Joffe, Appl. Cat. 20 (1986) 215;
(y) B. Nkosi, M.D. Adams, N.J. Coville, G.J. Hutchings, J. Catal. 128 (1991) 378.
[11] (a) H. Schmidbaur (Ed.), Gold: Progress in Chemistry, Biochemistry and Technology, Wiley, Chichester, 1999;
(b) H. Schmidbaur, Gold Bull. 23 (1990) 11.
[12] E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, Angew. Chem. Int. Ed. 41 (2002) 4563.
[13] (a) N.C. Baenziger, W.E. Bennet, D.M. Soboroff, Acta Crystallogr. B 32 (1976) 962;
(b) K. Angermaier, E. Zeller, H. Schmidbaur, J. Organomet. Chem. 472 (1994) 371;
(c) A.K. Al-Sa'ady, C.A. McAuliffe, R.V. Parish, J.A. Sandbank, Inorg. Synth. 23 (1985) 191;

(d) H. Schmidbaur, B. Brachthäuser, S. Gamper, A. Schier, O. Steigelmann, Z. Naturforsch. 47b (1992) 1725.

[14] Imta, Junichi, Saito, Junji, Ueda, Takashi, Jpn. Kokai Koho, JKXXAF JP 05213854 A2 19930824 (1993), to Mitsui Petrochemical Ind., Japan.

[15] (a) P. Roembke, A. Schier, H. Schmidbaur, J. Chem. Soc., Dalton Trans. (2001) 2482;
(b) P. Roembke, A. Schier, H. Schmidbaur, Z. Naturforsch. 57b (2002) 605;

(c) P. Roembke, A. Schier, H. Schmidbaur, Z. Naturforsch. 58b (2003) 168;
(d) P. Roembke, A. Schier, F. Wiesbrock, H. Schmidbaur, Inorg. Chim. Acta 347 (2003) 123;
(e) P. Roembke, A. Schier, H. Schmidbaur, S. Cronje, H. Raubenheimer, Inorg. Chim. Acta, 357 (2004) 237.

[16] M. Preisenberger, A. Schier, H. Schmidbaur, J. Chem. Soc., Dalton Trans. (1999) 1645.