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Regio- and Stereoselective Intermolecular Hydroalkoxylation of Alkynes Catalysed by Cationic Gold(I) Complexes

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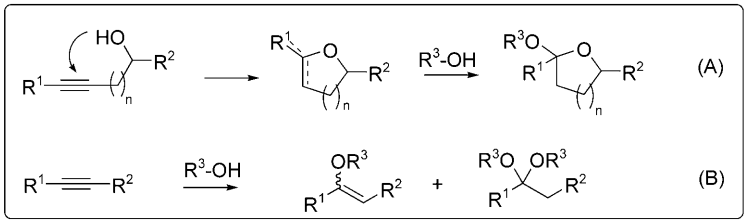
Abstract: Vinyl ethers and ketals are obtained from the reaction of phenylacetylene derivatives and dimethyl acetylenedicarboxylate (DMAD) with alcohols in good yields and levels of stereoselectivity by using cationic gold(I)-phosphine complexes as catalysts. By choosing the appropriate phosphine, the selective formation of the *Z* or the *E* isomer of the vinyl ether can be tuned, and the undesired formation of the ketal can be controlled. The isomerisation of fumarates (*Z*-isomer) to maleates (*E*-isomer) is a gold-catalysed process that can be conducted in one-pot. When using polyols, 5-membered cyclic ketals are easily isolated by extraction with hexane and the gold complex can be reused.

Keywords: alkynes; calalyst recovery; catalysis; enol ethers; gold; hydroalkoxylation

Introduction

The addition of alcohols to alkynes, the so-called hydroalkoxylation (Figure 1), is a 100% atom-economic reaction that gives direct access to vinyl ethers and ketals,[1a] and the intermolecular addition to acetylene has industrial applications.[1b] These reactions are traditionally performed under metal-catalysed conditions since, otherwise, the addition is extremely slow or the conditions are too harsh.



Ligand Complex

- **A** $AuPPh_3NTf_2$ **1a**
- **B** $AuP[(trisCF_3)C_6H_2]_3NTf_2$ **1b**
- **C** $AuDavePhosNTf_2$ **1c**
- **D** $AuSPhosNTf_2$ **1d**
- **E** $AuP(t\text{-}Bu)_3NTf_2$ **1e**

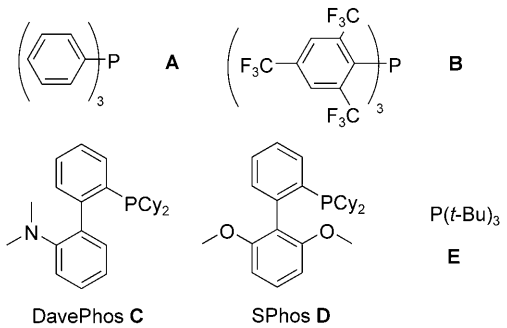


Figure 1. Intramolecular (A) and intermolecular (B) hydroalkoxylation of alkynes (top); gold(I) complexes used as catalysts in this work (bottom).

The intramolecular hydroalkoxylation is clearly favoured over the intermolecular version, and many different metals have been reported as efficient catalysts for intramolecular hydroalkoxylations under mild conditions.[1a,2] However, this is not the case for intermolecular hydroalkoxylations. Indeed, although different metals,[3] including palladium,[4,5] platinum,[6] mercury,[7] ruthenium,[8] copper,[9] silver,[10] zinc[11] and gold[12] have been used as catalysts, none of them fulfill the levels of efficiency, mildness and selectivity achieved for the intramolecular version. Therefore, to find selective, efficient and environmentally friendly[13] procedures for the intermolecular hydroalkoxylation of alkynes is of huge interest. In such a case, a successful procedure should accomplish the following: (i) selective monoaddition of the alcohol to the alkyne and (ii) stereocontrol on the final vinyl ether (for internal alkynes). Concerning the first issue, the literature shows that controlling a monoaddition mode is difficult as alkynes generally prefer a twofold addition mode, affording ketals instead of vinyl ethers.[11,12,14] Alkyl propiolates make an exception to this trend, as their resulting vinyl enol ethers are stable enough to avoid a second alcohol addition. Nevertheless, two isomers, i.e., *E*: maleates and *Z*: fumarates can be produced and, consequently, the addition of alcohols to alkyl propiolates is a convenient reaction to test for catalyst stereoselectivity. Different metal catalysts have been reported to perform the hydroalkoxylation of alkyl propiolates, such as lead,[15] palladium,[5,16] silver,[10] iridium[17] and molybdenum.[18] However, fumarates were always the major or exclusive products, coming from a *trans*-addition of the alcohol across the triple bond. The only scarce examples where maleates were the major products correspond to a stoichiometric addition of metal alkoxide complexes (metal: Mn, Mo, Re)[19] to DMAD and two amine-catalysed additions.[20]

Given the greater difficulty to accomplish the intermolecular process relative to its intramolecular version, stronger Lewis acids are required to improve the reaction rate. This hypothesis is clearly corroborated by listing the different catalysts found in previous reports for intermolecular hydroalkoxylations, that involve highly acidic metal salts containing a weakly-coordinating counteranion such as OTf^-,[6,9,10] BF_4^-,[5] or PF_6^-,[4,6] either as the pure compound or formed *in-situ* from a pre-catalyst. Taking this into account, we thought that phosphine-gold(I) complexes bearing the low coordinating group NTf_2^- (Figure 1), which are cationic and highly acidic isolable compounds that can be used as catalysts in different processes involving alkyne activation,[21,22] could be an active and selective catalyst for performing the hydroalkoxylation of alkynes. In the present work, we will show that these phosphine-gold(I) complexes are indeed regio- and stereoselective catalysts for this transformation. The monoaddition mode on terminal and internal alkynes is in most cases strongly favoured, so vinyl ethers are selectively formed. In the case of alkyl propiolates, the stereoselectivity can be switched by choosing the appropriate conditions, and the corresponding maleates can be efficiently obtained for the first time by a metal-catalysed hydroalkoxylation. In addition, these gold(I) complexes are highly insoluble in hexane, which enables quantitative recovery by precipitation after the reaction and efficient reuse.

Results and Discussion

Catalyst Screening and Substrate Scope

To catalyse the hydroalkoxylation of alkynes, gold(I) complexes containing various electron-withdrawing (EWD, complexes **1a** and **1b**) and electron-donating phosphines (ED, complexes **1c–1e**) have been prepared (see Figure 1 and Experimental Section), and reactivity results using phenylacetylene **2** as the test alkyne and 2 mol% catalyst loadings are given in Table 1.[23]

It can be seen there that, when **2** was reacted with *n*-butanol **3**, gold(I) complexes **1a** and **1b** give a high ratio of enol ether **4** to ketal **5** (entries 1 and 2), showing that a nearly complete selectivity to the monoaddition product is achieved when using complexes containing the EWD phosphines. Complexes containing the ED phosphines **1c–e** were also highly active catalysts which, conversely to their more electrophilic counterparts **1a** and **1b**, led predominantly to the ketal product **5** (entries 3–5). Although it is true that catalyst **1d** is more active than **1a** (compare entries 9 and 10), the ketalisation takes place with the former at a higher rate than the hydroxyalkoxylation does, since **4** and **5** are formed concominantly even when using 1 equivalent of **3**. Therefore, the high selectivity achieved by catalysts **1a** and **b** for the enol ether **4** is remarkable and does not come from a kinetic control. A catalyst with lower Lewis acidity, such as the gold(I) complex having Cl^- as counteranion instead of the low-coordinating NTf_2^-, gave no conversion at all (entry 6). The presence of the phosphine ligand in the catalyst is necessary (entry 7). Importantly, it has to be pointed out that the reaction is not Brønsted acid-catalysed (entry 8).

The preliminary scope of the reaction was explored by surveying an array of alkynes (Table 2). Both terminal (entries 1 and 2) and internal (entries 3–5) aromatic alkynes reacted well in this Au(I)-catalysed hydroalkoxylation, although variable and non-negligible amounts of ketals and ketones were produced along with the desired vinyl enol ethers. Moreover, terminal alkyl alkynes also reacted well, although ketals were the main product (entries 6 and 7, see also footnote

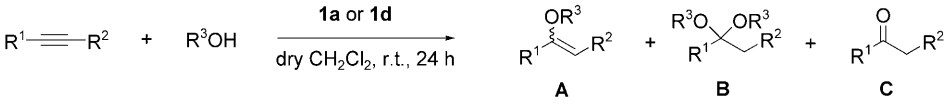
Table 1. Hydroalkoxylation of phenylacetylene **2** with *n*-butanol **3** catalysed by $AuPR_3NTf_2$ complexes **1a–e** and others.[a]

2 3 4 5

Entry	**3** [equiv.]	Catalyst	Conversion [%][b]	Ratio of **4/5** [%][c]
1	2	**1a**	98 [69]	88/5
2		**1b**	96	92/2
3		**1c**	>99	10/88
4		**1d**	98	34/63
5		**1e**	97	28/69
6		$AuPPh_3Cl$	0	–
7		$AuNTf_2$[d]	<1	–
8		$HNTf_2$	<1	–
9	1	**1a**	62	>99/1
10		**1d**[e]	74	50/50

[a] *Reaction conditions:* alkyne (1 mmol), alcohol (1–2 mmol), catalyst, dry solvent (0.5 mL), stirring at room temperature for 24 h.
[b] Average of two runs, calculated by GC; in brackets, isolated yield.
[c] Average of two runs; remaining to fit conversion corresponds to ketones from hydrolysis and/or direct hydration of the alkyne.
[d] Generated *in-situ* by stirring AuCl + $AgNTf_2$ for 10 min.
[e] 1 mol%.

Table 2. Scope of the hydroalkoxylation of different alkynes and alcohols catalysed by complex **1a** or **1d**.



A B C

Entry	R^1	R^2	Au Catalyst (mol%)	R^3OH (equiv.)	Conversion [%][a]	Product Distribution **A** (*Z*/*E*):**B**:**C** [%][a]
1	$PhOC_6H_4$	H	**1a** (2)	*n*-BuOH (2)	100	50 (–):0:48
2	ClC_6H_4	H	**1a** (2)	*n*-BuOH (2)	88	23 (–):34:38
3	Ph	Ph	**1a** (5)	*n*-BuOH (1)	57	43 (30/13):2:13
4				*n*-BuOH (2)	98	88 (60/28):3:7
5			**1d** (1)	*n*-BuOH (1)	62	30 (24/6):30:7
6	C_6H_{13}	H	**1a** (0.5)	MeOH (1)	42[b]	14 (–):86:0
7			**1a** (2)	MeOH (2)	100[b]	31 (–):69:0
8	Ph	*n*-Bu	**1a** (5)	*n*-BuOH[c] (1)	60	0:0:60
9				*i*-PrOH[c] (1)	58	messy mixture
10			**1d** (5)	*i*-PrOH (1)	61	messy mixture

[a] Determined by GC.
[b] Determined by NMR, see also Figure S11 and S12 in Supporting Information.
[c] Benzylic alcohols dehydrated to form the corresponding ethers under these experimental conditions.

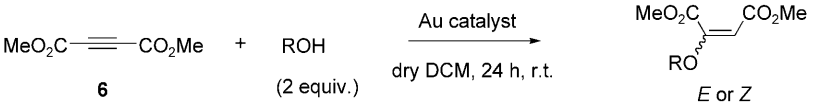
[b]). The vinyl ethers of alkyl derivatives were not stable enough under the acidic conditions and formed finally the corresponding ketones or uncontrolled by-products (entries 8–10).

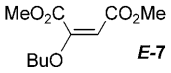
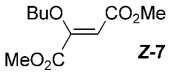
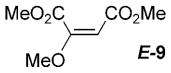
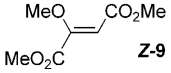
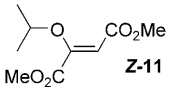
Stereoselective Synthesis of Vinyl Ethers

As commented before, alkyl propiolates are suitable alkynes to study the stereoselectivity of the reaction, since the corresponding vinyl ethers as *E* and *Z* isomers are stable. Thus, the addition of different alcohols to dimethyl acetylenedicarboxylate (DMAD) catalysed by complexes **1a–d** was tested (Table 3).

Remarkably, a different stereoisomer was obtained depending on the catalyst employed, i.e., catalysts with EWD phosphines **1a** and **1b** lead to butoxymaleate ***E*-7** (entries 1–3)[24] and catalysts with ED phosphines **1c** and **d** lead to the fumarate ***Z*-7** (entries 4 and 5), with high levels of stereoselectivity in both

Table 3. Hydroalkoxylation of DMAD **6** with different alcohols catalysed by $AuPR_3NTf_2$ complexes **1a–d**.[a]



Entry	ROH	Main Product	Catalyst (mol%)	Yield [%][b]	*Z*/*E*[c]
1	*n*-BuOH **3**	 *E*-**7**	**1a** (5)	>99 [99]	1/13[d]
2			**1a** (0.5)	58	1/1.1
3			**1b** (0.5)	29	1/4
4		 *Z*-**7**	**1c** (0.5)	89	8/1
5			**1d** (0.5)	>99 [87]	19/1[d]
6	MeOH **8**	 *E*-**9**	**1a** (5)	>99	1/19
7			**1d** (0.5)	>99	1/10
8		 *Z*-**9**	**1d** (0.05)	94	4.5/1
9	*i*-PrOH **10**	 *Z*-**11**	**1d** (5)	>99 [77]	99/1

[a] *Reaction conditions:* alkyne (1 mmol), alcohol (2 mmol), catalyst, dry solvent (0.5 mL), stirring at room temperature for 24 h.
[b] Average of two runs, calculated by GC; in brackets, isolated yield.
[c] Average of two runs.
[d] Gram scale.

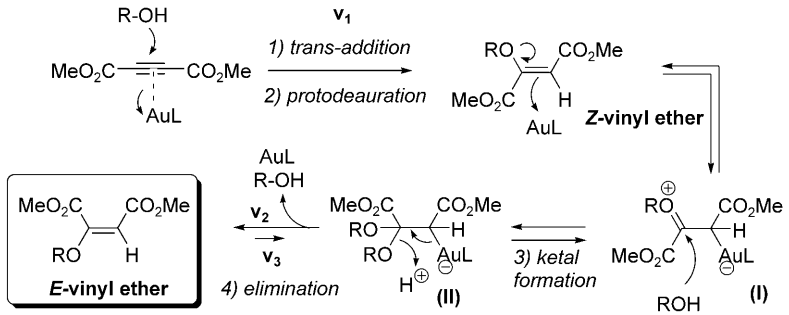
cases. Yields were excellent even at the gram scale (see entries 1 and 5). MeOH comparably displayed an enhanced reactivity profile, with a high-yielding access to the corresponding fumarate ***Z*-9** being possible at a remarkable low catalyst loading of 0.05 mol% (entry 8). Curiously, the amount of catalyst **1d** appeared to greatly influence the sense of stereoselectivity of the hydromethoxylation (compare entry 7 and entry 8), what would be explained ahead by isomerisation effects (for instance, see Figure S9 in the Supporting Information). A secondary alcohol such as *i*-PrOH added equally well with the achievement of excellent yield and virtually complete stereoselectivity (entry 9), though a larger amount of catalyst **1d** was required to complete the reaction (compare entries 5, 8 and 9), and tertiary alcohols do not react under our reaction conditions.

The reusability of catalyst **1a** was studied for the reaction of phenylacetylene **2** with *n*-BuOH **3** (entry 1 in Table 1, see Table S1 in the Supporting Information). Two procedures can be followed for recovering **1a**, depending on the solvent employed: with CH_2Cl_2, **1a** is recovered by precipitation in hexane and filtration, while if CH_3CN is used the reaction products are extracted with hexane, **1a** remaining in the CH_3CN phase. The inmiscibility of the acetonitrile phase in hexane is only possible because a rather high substrate concentration is used (see Supporting Information). Anyway, in both cases the results obtained are similar and the catalyst is still active after three uses, although a decrease in activity is observed. The ^{31}P NMR spectrum of the complex after the third use shows in both cases a new signal at 45 ppm, corresponding to the species[25] $[Au(PPh_3)_2]NTf_2$ (see Figure S1 in the Supporting Information). Unfortunately, this species is not active as catalyst. Catalyst **1d** deactivates similarly during the addition of *n*-BuOH **3** to DMAD **6** (see Table S2 and Figure S2 in the Supporting Information).

Insights into the Mechanism

A tentative mechanism for the addition of alcohols to the internal alkyne **6** catalysed by gold complexes **1a–e** is depicted in Scheme 1:

The different steps in the mechanism were investigated by kinetic and isotopic studies, and NMR experiments. The reaction starts with the formation of the primary *Z*-vinyl ether, which should take place by a gold(I)-catalysed *trans*-addition of the alcohol across the triple bond. The different catalytic activities of **1a** (EWD phosphine) and **1d** (ED phosphine), measured as the initial rate (r_1), were compared, and **1d** is one order of magnitude more active than **1a** (Table S3, see Figure S3 in the Supporting Information). In contrast, the isomerisation rate (r_2) is three times higher for catalyst **1a** compared to **1d** (Table S3, see Figure S4 in the Supporting Information), and equals to r_1 for **1a** ($r_1/r_2 = 1.1$, Table S3 in the Support-



Scheme 1. Proposed mechanism for the gold(I)-catalysed formation of dimethyl fumarates and maleates from DMAD **6** and alcohols.

ing Information). This result nicely explains why ***E*-7** is formed when **1a** is used as catalyst and not when **1d** is used instead (Figure S5 in the Supporting Information). The reverse isomerisation, from ***E*-7** to ***Z*-7**, is negligible for both catalysts (Figure S6, r_3 in Table S3 in the Supporting Information). It should be remarked that the isomerisation is not catalysed by a Brønsted acid ($HNTf_2$, Figure S7 in the Supporting Information) and that the complex **1a** without the alcohol does not produce the isomerisation either (Figure S8 in the Supporting Information). From these results it can be concluded that the addition of the alcohol to the triple bond and subsequent isomerisation are catalysed by gold(I). The formation of the intermediate ketal was confirmed by NMR and kinetic experiments. The ketal corresponding to **7** (intermediate **II** in Scheme 1, R = *n*-Bu) was found in small amounts in the ^{1}H NMR spectrum of the reaction mixture, peaking as a singlet at 2.95 [$CO_2Me{-}CH_2{-}C(OBu)_2CO_2Me$]. The vinyl ether ***E*-12** was smoothly achieved by addition of CD_3OD to ***Z*-7** (Figure 2), which unambiguously comes from a transalkoxylation process.

Following the first pathway (Scheme 2, **PW-1**), and using CD_3OD instead of MeOH, one should expect that the obtained vinyl ethers contain deuterium at the double bond (see above Figure 2). However, no deuterium was found in the product, as assessed by ^{1}H (correct integration for all the protons), ^{13}C NMR (no splitting of the peak corresponding to the olefinic carbon) and GC-MS (no +1 peaks). Thus, the double bond regeneration should come from the release of one of the alcohols and gold, the olefinic proton remaining untouched during this process. If we consider

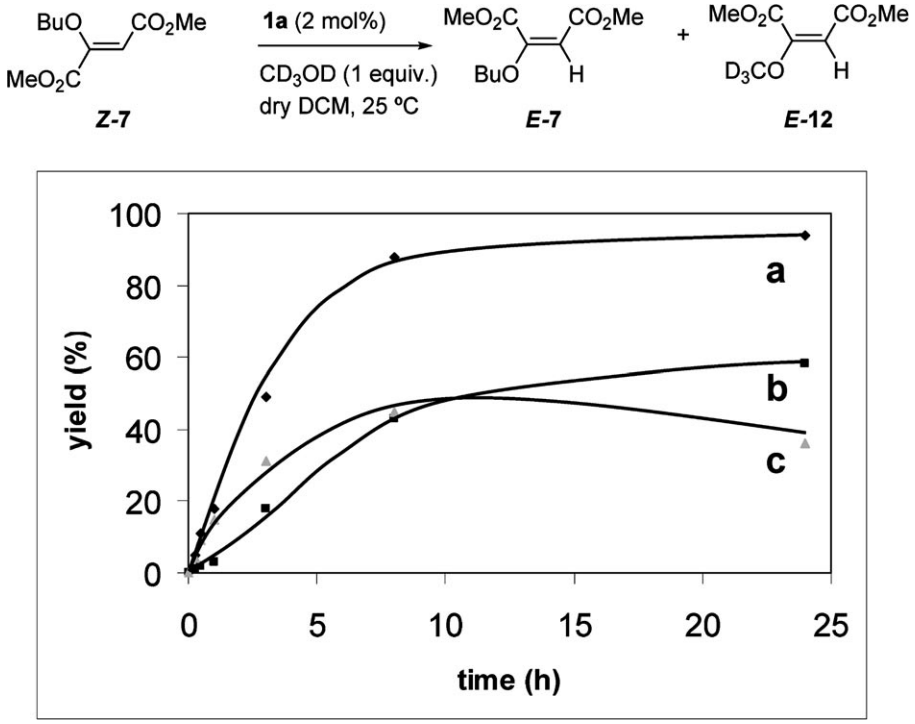
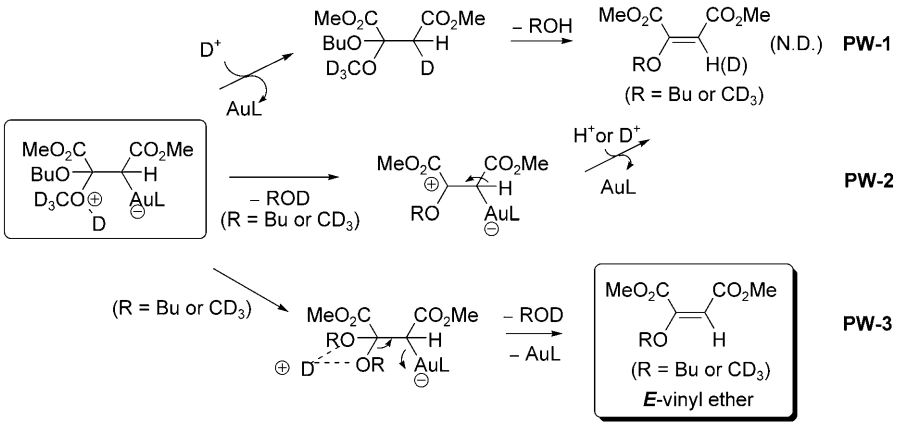


Figure 2. Plot-time yield for the isomerisation of **Z-7** to the sum of both *E*-isomers (**a**), to ***E*-7** (**b**) and to ***E*-12** (**c**).



Scheme 2. Proposed ways for the elimination step.

PW-2, the presence of deuterium at the double bond should also be expected and, consequently, this pathway can be rejected. Finally, taking into account the kinetic and isotopic results, **PW-3** was considered as the plausible elimination mechanism.

Although the kinetic approach shown here could be considered incomplete, our conclusions are also supported from the product distribution and the isotopic results. We do not know if the elimination is a sequential E_1 mechanism-type (ROH releases first, generates a carbocation, and then gold eliminates) or concerted. However in either case, gold should persist all over the isomerisation process. In fact, gold may exert a directing effect, forcing the two CO_2Me to be eclipsed in the transition state and forming the maleate adduct after deauration. This directing effect of the gold complex could be due to steric hindrance and/or to coordination to the opposite OR groups.

As it has been seen before, the isomerisation rate from the *Z* to the *E* isomer changes dramatically as a function of the catalyst employed (see Table S3 and Figure S5 in the Supporting Information), allowing us in this way to control the stereoselectivity of the final product. To this respect, a further study was carried out to probe the influence of other parameters such as the amount of catalyst and alcohol on the yield and selectivity of the reaction (Figure S9 in the Supporting Information). It was found that the reaction rates for both processes, hydroalcoxylation and isomerisation, are accelerated by increasing the amount of catalyst and the alcohol concentration (see Tables S4–S6 as well in the Supporting Information). This explains why catalyst **1d** is able to form the *Z* or the *E* isomer, depending on the reaction conditions (see Table 3, compare entries 7 and 8). As MeOH is *ca.* 10 times more reactive than *n*-BuOH, ***E*-9** is eventually formed with the same amount of catalyst **1d** (see Table 3, compare entries 5 and 7). In general, the results observed in Table 3 are in good agreement with this study. It has to be remarked that **1d** keeps its activity after storage for six months (Table S4, entry 6 in the Supporting Information).

Regioselective Hydroalkoxylation with Polyols

The particular behaviour of the gold(I) catalysts **1a–e** in terms of selectivity prompted us to study a possible regioselective addition of diols to alkynes. Moreover, the hydrolysis of the ketals would lead to the corresponding ketones, which represent a formal regioselective hydration of alkynes, an issue which is still unresolved. The results obtained are listed in Table 4.

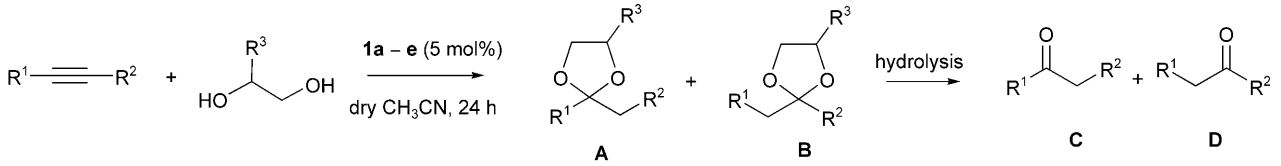
Complex **1e** was the best catalyst (compare entries 1–7 with 8–12), showing complete conversion and selectivity for the addition of glycerol to phenylacetylene (entry 7).[26] As far as we know, no hydroalkoxylations of alkynes with glycerol have been previously reported.[27] Glycerol is more active than the diols (compare entries 12, 13 and 15) and the 5-membered ketal was exclusively formed in all cases. CH_3CN was the solvent of choice at room temperature since glycerol is not soluble in CH_2Cl_2 or toluene (entry 3). Good regioselectivities were obtained in some cases (5–3 to 1, see entries 11–15), although at low conversions. Unfortunately, the regioselectivity obtained for the corresponding ketones after acidic hydrolysis was low (higher: 2.5 to 1 in entry 11).

Catalyst Recovery and Recycling

The recovery and reuse of homogeneous gold catalysts is of interest from an economical and environmental point of view. Complex **1a** could be reused for the addition of glycerol **13** to phenylacetylene **2** up to six times without depletion of the catalytic activity (Figure 3).

As observed before for the formation of vinyl ethers, the reaction mixture including catalyst **1a** be-

Table 4. Au(I)-catalysed formation of cyclic ketals from alkynes and polyols and subsequent hydrolysis.[a]



Entry	R^1	R^2	R^3	Catalyst	T [°C]	Conversion [%][b]	**A** [%][b]	**B** [%][b]	**C** [%][b]	**D** [%][b]
1	Ph	H	CH_2OH	$AuPPh_3BF_4$[c]	20	30	30	–	30	–
2				$AuPPh_3Cl$		0	-	–	-	–
3				**1a**[d]		90	90	–	90	–
4				**1b**		>99	87	–	99	–
5				**1c**		0	-	–	-	–
6				**1d**		90	84	–	90	–
7				**1e**		**98**	**92**	–	98	–
8	Ph	*n*-Bu	CH_2OH	**1a**	80	6	1	3	2	4
9				**1b**		24	6	9	13	11
10				**1c**		15	2	7	5	10
11				**1d**		29	**3**	**16**	**8**	**21**
12				**1e**		**65**	17	33	30	35
13			H	**1e**		50	14	27	22	28
14				**1c**		14	3	11	5	9
15			Et	**1e**		29	7	22	12	17
16				**1c**		3	1	2	1.5	1.5

[a] *Reaction conditions:* alkyne (0.25 mmol), diol (0.25 mmol), catalyst (0.05 mmol), $AgBF_4$ (if necessary, 0.05 mmol), dry solvent (0.25 mL), N_2.
[b] Calculated by GC, 3:1 mixture of diastereoisomers.
[c] Formed *in-situ*.
[d] The reaction did not work in dry CH_2Cl_2 or dry toluene as solvents.

haves as an ionic liquid when dissolved in CH_3CN, allowing extraction of the reaction products in hexane. Ionic liquids have been used as reaction medium for gold-catalysed reactions before (including recycles).[28] ICP Au analyses of **14** show that the amount of gold leached in the extraction procedure is less than 0.05%. In accordance, the ^{31}P NMR spectrum of the catalytic species recovered after the sixth use showed the persistence of the phosphine ligands (see Figure S10 in the Supporting Information), although, again, $[Au(PPh_3)_2]NTf_2$ was the major species detected. Nevertheless, the catalytic system remains active for this particular reaction.

Conclusions

$AuPR_3NTf_2$ complexes **1a–e** are selective catalysts for the intermolecular hydroalkoxylation of electron-poor alkynes of type R−C≡C−EWG and DMAD. In the reactions of phenylacetylene, the ratio vinyl ether to ketal can be controlled by choosing the catalyst. When using stabilised internal alkynes such as DMAD, both *Z:E* isomers of the vinyl ether can be obtained with excellent yields and stereoselectivities, depending on the catalyst employed and the reaction conditions. The *E* isomer comes from a gold-catalysed isomerisation of the *Z* counterpart, which is initially formed through an expected *trans*-hydroalkoxylation mechanism. Given the plethora of studies arising in the last years on C=C activation by gold, these findings can be of interest.

Moderate to good levels of conversion and selectivity are achieved when using polyols as hydroalkoxylating agents. The complex **1a** is reused up to six times without an observed decrease of the catalytic activity for phenylacetylene.

The tuneable selectivity shown by catalysts **1a–e** together with the recovery of **1a**, the easy isolation of the products and the mild conditions employed render the procedure reported here a convenient process from synthetic and environmental points of view.

Experimental Section

Typical Preparation of the Gold(I) Catalysts [AuDavePhosNTf$_2$ (1c)]

AuDavePhosCl (350 mg, 0.56 mmol, see Supporting Information for preparation) and $AgNTf_2$ (217 mg, 0.56 mmol) were placed in a round-bottomed flask. Air evacuation-nitrogen refilling cycles were carried out and a rubber septum was rapidly fitted after the last nitrogen refilling, a nitrogen balloon was additionally coupled through a needle. Then,

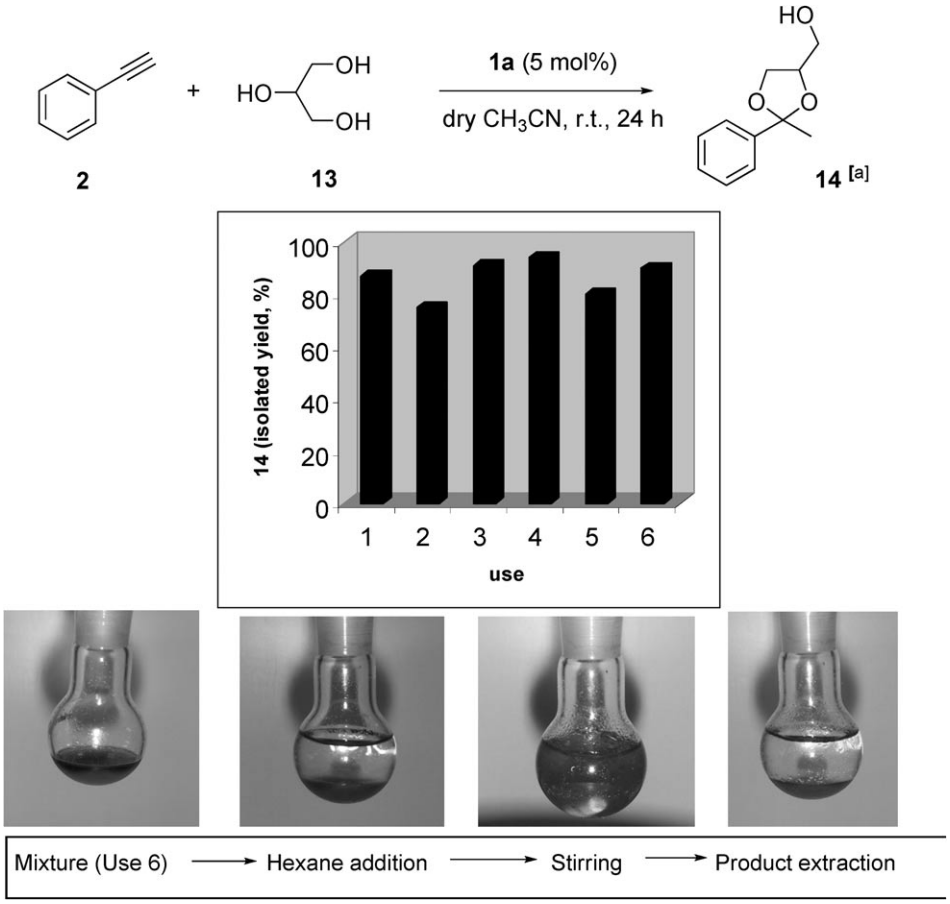


Figure 3. Reusability study of **1a** dissolved in CH_3CN as "ionic liquid-type" system.[a] 3:1 mixture of diastereoisomers.

dry CH_2Cl_2 (15 mL) was added and the mixture was magnetically stirred at room temperature for 30 min. Then, the white solid formed (AgCl) was filtered off over celite and the clear filtrates were concentrated to dryness to obtain AuDavePhosNTf$_2$ as a yellow-bright solid; yield: 490 mg (quantitative). IR: $\nu = 2931$, 2854, 1342, 1196, 1142, 1057 cm^{-1}; ^{1}H NMR: $\delta = 7.64$–7.38 (5H, mult), 7.11 (2H, t, $J = 7.7$ Hz), 6.99 (1H, d, $J = 7.0$ Hz), 2.46 (6H, s), 2.28–2.00 (4H, mult), 1.86–1.62 (8H, mult), 1.48–1.18 (10H, mult); ^{13}C NMR: $\delta = 151.2$ (C), 148.1 (C,), 133.4 (CH), 132.4 (CH,), 131.6 (CH, ×2), 129.3 (CH), 127.3 (CH), 124.0 (C), 123.3 (C,), 122.2 (CH), 119.4 (C, $J_{C,F} = 323$ Hz), 119.1 (CH), 43.4 (CH_3, ×2), 37.4 (CH, $J_{C,P} = 34$ Hz), 36.3 (CH, $J_{C,P} = 34$ Hz), 31.0 (CH_2), 29.6 (CH_2,), 26.6 (CH_2), 26.5 (CH_2, ×2), 26.4 (CH_2), 26.3 (CH_2), 25.6 (CH_2), 25.5 (CH_2, ×2); ^{31}P NMR: $\delta = 39.1$; anal. calcd. for $C_{28}H_{36}AuF_6N_2O_4PS_2$: C 38.63, H 4.17, N 3.22, S 7.37; found: C 39.53, H 4.32, N 3.24, S 7.43; HR-MS (ESI): $m/z = 590.2258$, $(M-Cl)^+$, major peak; calcd. for $C_{26}H_{36}AuNP$: 590.2251.

Typical Hydroalkylation Procedure with Monoalcohols (Table 3, entry 1)

Complex **1a** (39 mg, 5 mol%) was placed in an oven-dried vial and dry CH_2Cl_2 (0.5 mL), but-2-ynedioic acid dimethyl ester **6** (DMAD, 122 μL, 1 mmol) and *n*-butanol **3** (182 μL, 2 mmol) were sequentially added. The vial was rapidly sealed and the mixture was magnetically stirred at room temperataure for 24 h. Then, an aliquot was taken for GC analysis and the mixture was added to *n*-hexane (50 mL) and stirred for 5 min. The resulting suspension was cooled in the fridge for 1 h and, after this time, it was left to reach room temperature and filtered over celite. The filtrates were concentrated under reduced pressure to give *E*-2-butoxybut-2-enedioic acid dimethyl ester ***E*-7** as a colourless liquid; yield: 184 mg (85%, *E*/*Z* ratio = 10:1). GC/MS: $m/z = 216$ ($M^{+\cdot}$, 2%), 201 (2%), 185 (4%), 173 (2%), 129 (31%), 101 (100%), 69 (45%); ^{1}H NMR: $\delta = 5.10$ (1H, s), 3.80 (3H, s), 3.79 (2H, t, $J = 6.5$ Hz), 3.61 (3H, s), 1.66 (2H, tt, $J = 7.5$ Hz, 6.5 Hz), 1.35 (2H, sext, $J = 7.5$ Hz), 0.86 (3H, t, $J = 7.5$ Hz); ^{13}C NMR: $\delta = 66.2$ (C), 163.9 (C), 162.0 (C), 92.6 (CH), 69.8 (CH_2), 52.6 (CH_3), 51.2 (CH_3), 30.1 (CH_2), 18.7 (CH_2), 13.4 (CH_3).

Reusability Study using Glycerol as Alcohol (Figure 3)

Complex **1a** (78 mg, 5 mol%) and glycerol **13** (184 mg, 2 mmol) were placed in an oven-dried 10 mL round-bottomed flask. Air evacuation-nitrogen refilling cycles were carried out and a rubber septum was rapidly fitted after the last nitrogen refilling, a nitrogen balloon was additionally coupled through a needle. Then, dry CH_3CN (1 mL) and phenylacetylene **2** (330 μL, 3 mmol) were sequentially added and the mixture was magnetically stirred at room temperature for 24 h. Then, *n*-hexane (10 mL) was added

and the mixture stirred for 15 min. After stopping, the top layer (hexane) was separated with a pipette and fresh *n*-hexane (10 mL) was added and the mixture stirred again for 5 min. This process was repeated once again. In one run, the remaining catalyst was dried under vacuum for 1 h and fresh reactants and solvent (see above) were added to perform a new reaction. In the other run, an aliquot was taken from the combined hexane extracts and analysed by GC. Then, volatiles were removed under vacuum and the resulting residue was purified by a rapid column chromatography (50% AcOEt/hexane) to give 2-methyl-2-phenyl-[1,3]dioxolan-4-yl)-methanol **14**; yield: 338 mg (87%, 3:1 mixture of diastereoisomers, only major diastereoisomer shown). R_f (neat AcOEt): 0.47. GC/MS: *m/z* (M^+ 194) = 179 (100%), 163 (10%), 105 (79%), 77 (29%), 43 (31%); IR: ν = 3421 (b), 2988, 2934, 2888, 1446, 1374, 1246, 1201, 1135, 1046, 1026, 940, 880, 762, 703 cm^{-1}); ^1H NMR: δ = 7.40 (2H, mult), 7.24 (3H, mult), 3.99 (1H, mult), 3.77 (1H, dd, J = 8.1 Hz, 5.4 Hz), 3.69 (2H, tt, J = 8.4 Hz, 7.1 Hz), 3.55 (1H, dd, J = 11.6 Hz, 5.3 Hz), 2.30 (1H, s), 1.60 (3H, s); ^{13}C NMR: δ = 142.9 (C), 128.2 (CH, ×2), 125.2 (CH, ×2), 124.7 (CH), 109.6 (C), 76.0 (CH), 65.7 (CH_2), 63.3 (CH_2), 28.0 (CH_3); anal. calcd. for $C_{11}H_{14}O_3$: C 68.02, H 7.27; found: C 66.88, H 7.67; HRMS (ESI): *m/z* 195.1014 [$(M+H)^+$, calcd. for $C_{11}H_{15}O_3$: 195.1021], 193.0879 [$(M-H)^+$, calcd. for $C_{11}H_{13}O_3$: 193.0865], 179.0668 [$(M-H-CH_3)^+$, major peak, calcd. for $C_{10}H_{11}O_3$: 179.0708].

Supporting Information

The syntheses of gold catalysts **1b** and **1c**, reaction procedures, compound characterisation, NMR spectra and additional Tables and Figure for this article are available as Supporting Information.

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