Palladium-catalyzed cycloisomerization of (*Z*)-enynols into furans using green solvents: glycerol *vs.* water†

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Heteroannulation reactions of (*Z*)-2-en-4-yn-1-ol derivatives into furans can be conveniently performed in water and glycerol using *cis*-[PdCl$_2$(DAPTA)$_2$] as catalyst. Higher activities were observed in an aqueous medium, but catalyst recycling was much more effective in glycerol.

Chemical transformations are experiencing a deep change to meet sustainability criteria imposed by the Green Chemistry principles.[1] In this sense, one of the crucial points in realizing a "green chemical" process involves the choice of a safe, non-toxic and cheap solvent.[2] Water has been, for a long time, the first solvent of choice regarding the aforementioned considerations. Indeed, it is now well-accepted that water is a reliable alternative to the organic, petroleum-based, solvents commonly used in chemical laboratories and industry.[2] Innumerable examples illustrating the utility of water in stoichiometric and catalytic organic synthesis have been described in the literature during the last two decades.[3]

On the other hand, the large surplus of glycerol, generated as the main byproduct (≈10% by weight) of the biodiesel production process, has recently led to a collapse in prices which has been accompanied by a growing imbalance in the supply/demand of this chemical. Therefore, finding new applications for glycerol as a low-cost raw material has become an urgent necessity.[4] One possible application of glycerol is its use as a green reaction medium. In fact, as recently suggested by Jérôme and co-workers,[5] glycerol can be considered as "organic water" since, like water, it is abundant, biodegradable, inexpensive, non-toxic, highly polar, immiscible with hydrocarbons, able to form strong hydrogen bonds and to dissolve inorganic compounds (salts, acids, bases and transition metal complexes). In addition, compared to water, it has the advantage of its higher boiling point, lower vapor pressure, and that it is able to dissolve organic compounds usually immiscible with water. However, despite its great potential as an environmentally friendly solvent, there are currently very few synthetic processes described in the literature where glycerol is used as the reaction medium.[5,6] In particular, concerning the field of metal-catalysis, the only known examples relate to Heck and Suzuki couplings,[7] hydrogenation[8] and transfer-hydrogenation reactions,[9] and the ring closing metathesis of diolefins.[10]

Metal-catalyzed cycloisomerization of (*Z*)-2-en-4-yn-1-ol derivatives represents an attractive and atom-economic route to furans, which are important structural motifs present in many biologically active molecules and pharmaceutical substances, as well as versatile building blocks in synthetic organic chemistry.[11] Several Group 8–11 metal complexes have been successfully employed to promote these heteroannulation reactions in organic media, with palladium-, ruthenium- and gold-based catalysts showing the best performances.[12] However, despite its great synthetic interest, efforts devoted to develop this process in alternative media have been scarce.[13] Herein, we would like to communicate that the cycloisomerization of (*Z*)-2-en-4-yn-1-ols can be conveniently performed in glycerol and water using the hydrophilic Pd(II) complexes *cis*-[PdCl$_2$L$_2$] (L = PTA (**1**), PTA-Bn (**2**), DAPTA (**3**)) as catalysts (see Fig. 1).[14,15]

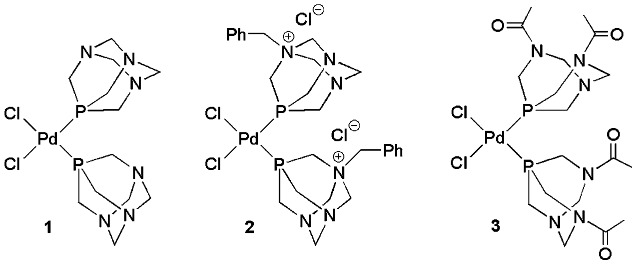

Fig. 1 Structure of the hydrophilic Pd(II) catalysts used in this study.

Firstly, using the cycloisomerization of commercially available (*Z*)-3-methyl-2-penten-4-yn-1-ol into 2,3-dimethylfuran as a model reaction, we compared the efficiency and selectivity of these Pd-catalysts in glycerol and water. Experiments were performed at room temperature, employing 2 mmol of the (*Z*)-enynol (1 M solution) and a metal loading of 0.2 mol%. The results obtained are collected in Table 1.

As shown in the table, regardless of the solvent employed, all of the compounds tested led to the selective and almost quantitative formation (≥96% GC yield) of the desired furan after 3–9 h of stirring at r.t. (entries 1–6). However, the reactions proceeded in all cases significantly faster in water than in glycerol (entry 2 *vs.* 1, 4 *vs.* 3 and 6 *vs.* 5). From this catalyst screening, complex *cis*-[PdCl$_2$(DAPTA)$_2$] (**3**) emerged as the top choice due to its high efficiency (99% GC-yield after 5 or 3 h; entries 5–6). In addition, the reaction rate could be significantly improved by increasing the working temperature to 75 °C. Under these new reaction conditions, using the same metal loading (0.2 mol% of **3**), 2,3-dimethylfuran was formed in 99% GC-yield after only 15–20 min of heating (entries 7–8).

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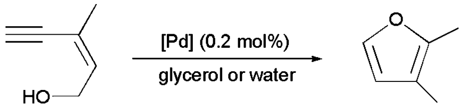
† Electronic supplementary information (ESI) available: Copies of the ^{1}H NMR and GC-MS spectra of all isolated furans, as well as gas chromatographs of the reactions collected in Table 2. See DOI: 10.1039/c0gc00169d

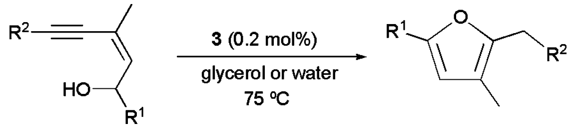
Table 1 Pd-catalyzed cycloisomerization of (*Z*)-3-methyl-2-penten-4-yn-1-ol in environmentally friendly media[a]



Entry	Catalyst	Solvent	Temp.	Time	Yield[b]	TOF[c]
1	**1**	glycerol	r.t.	9 h	96%	53 h^{-1}
2	**1**	water	r.t.	5 h	98%	98 h^{-1}
3	**2**	glycerol	r.t.	9 h	97%	54 h^{-1}
4	**2**	water	r.t.	5 h	97%	97 h^{-1}
5	**3**	glycerol	r.t.	5 h	99%	99 h^{-1}
6	**3**	water	r.t.	3 h	99%	165 h^{-1}
7	**3**	glycerol	75 °C	20 min	99%	1485 h^{-1}
8	**3**	water	75 °C	15 min	99%	1980 h^{-1}

[a] Reactions performed under N_2 atmosphere using 2 mmol of substrate (1 M solution in glycerol or water). [enynol : Pd] ratio = 500 : 1. [b] Determined by GC. [c] Turnover frequencies ((mol product/mol Pd)/time) were calculated at the indicated time.

Table 2 Cycloisomerization of (*Z*)-2-en-4-yn-1-ols catalyzed by *cis*-[$PdCl_2(DAPTA)_2$] (**3**) in environmentally friendly media[a]



Entry	Substrate (R^1/R^2)	Solvent	Time	Yield[b]	TOF[c]
1	H/H	glycerol	20 min	99% (84%)	1485 h^{-1}
2	H/H	water	15 min	99%	1980 h^{-1}
3	^{n}Bu/H	glycerol	2 h	99% (86%)	247 h^{-1}
4	^{n}Bu/H	water	2 h	99%	247 h^{-1}
5	Ph/H	glycerol	2 h	95% (83%)	237 h^{-1}
6	Ph/H	water	2 h	97%	242 h^{-1}
7	$CH_2C(Me){=}CH_2$/H	glycerol	2 h	99% (90%)	247 h^{-1}
8	$CH_2C(Me){=}CH_2$/H	water	2 h	99%	247 h^{-1}
9[d]	H/Ph	glycerol	24 h	88% (77%)	3 h^{-1}
10[d]	H/Ph	water	24 h	92%	4 h^{-1}

[a] Reactions performed at 75 °C under N_2 atmosphere using 2 mmol of substrate (1 M solution in glycerol or water). [enynol : Pd] ratio = 500 : 1. [b] Determined by GC (isolated yields in brackets). [c] Turnover frequencies ((mol product/mol Pd)/time) were calculated at the indicated time. [d] Reactions performed using 1 mol% of complex **3**. [enynol : Pd] ratio = 100 : 1.

Complex *cis*-[$PdCl_2(DAPTA)_2$] (**3**) was also effective in the selective cycloisomerization of other (*Z*)-enynols both in glycerol and water, thus confirming the generality of the process.[16] As shown in Table 2, replacement of the hydrogen atom (entries 1–2) by alkyl (entries 3–4), aryl (entries 5–6) or alkenyl (entries 7–8) groups at C-1 of the 3-methyl-2-penten-4-yn-1-ol skeleton was compatible with the cyclization conditions, the corresponding furans being generated in excellent GC yields (≥95%) after 2 h of heating at 75 °C. Heteroannulation of (*Z*)-3-methyl-5-phenyl-2-penten-4-yn-1-ol, bearing an internal C≡C bond, was also conveniently accomplished in glycerol and water (entries 9–10). However, a higher catalyst loading (1 mol%) was required in these cases. Remarkably, the high boiling point of glycerol allowed the isolation of the final products (77–90% yield) by Kügelrohr distillation of the crude reaction mixtures, thus circumventing the use of organic solvents.

The lifetime of a catalytic system and its level of reusability are very important factors.[17] In this sense, the hydrophilic character of *cis*-[$PdCl_2(DAPTA)_2$] allows it to be recycled easily after simple extraction of the final reaction product with immiscible diethyl ether (3 × 10 cm^3). Comparative results in glycerol and water using the cycloisomerization of (*Z*)-3-methyl-2-penten-4-yn-1-ol into 2,3-dimethylfuran as a model reaction are shown in Fig. 2. Thus, we have found that, while no appreciable loss of activity occurs in glycerol during five consecutive runs (96–99% GC-yields after 20 min), the efficiency of the aqueous solution decreases considerably after each recycling cycle, 24 h of heating being required in the fifth one to attain 91% of conversion. This different behavior of *cis*-[$PdCl_2(DAPTA)_2$] is not only related to it being more highly soluble in glycerol (3.1 mg cm^{-3}) than water (1.7 mg cm^{-3}),[18] but also to its stability in both media. In fact, although the homogeneity of the aqueous solution is apparently maintained after each cycle, decomposition of the catalyst *via* decoordination of the DAPTA ligand has been observed by $^{31}P\{^1H\}$ NMR spectroscopy.[19]

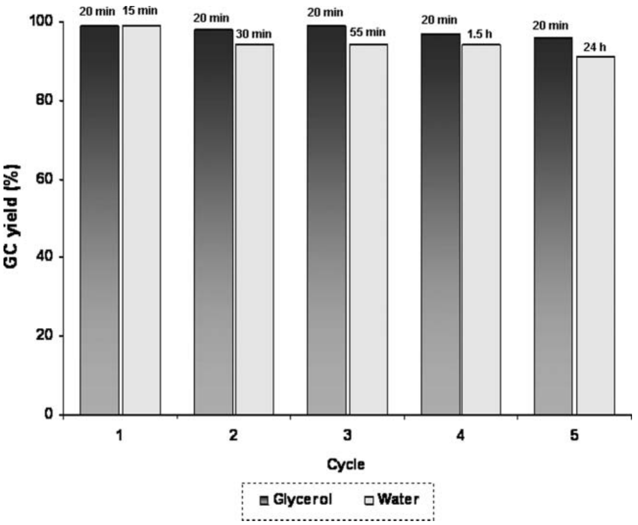
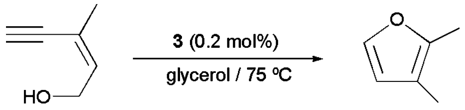


Fig. 2 Catalyst recycling in glycerol and water: reactions were performed as described in Table 2.

The excellent capability of the palladium/glycerol system to be recycled was further studied in depth. As shown in Table 3, the system could be recycled up to 17 times, leading to a cumulative TON value of 8190, the highest reported to date for this catalytic transformation.

In summary, we have demonstrated that, like water, glycerol can be employed as an environmentally friendly solvent for metal-catalyzed cycloisomerization reactions of (*Z*)-2-en-4-yn-1-ols into furans. The use of this low-cost and renewable feedstock, together with the highly effective catalyst recycling observed in glycerol, opens great prospects for developing more sustainable processes in the organic synthesis field. Further studies aimed at broadening the scope of this atom-economic transformation are currently in progress in our lab and will be presented in due course.

Table 3 Isomerization of (*Z*)-3-methyl-2-penten-4-yn-1-ol catalyzed by *cis*-[PdCl$_2$(DAPTA)$_2$] (**3**) in glycerol: catalyst recycling.[a]



Cycle	Time	Yield[b]	TON[c]	Cycle	Time	Yield[b]	TON[c]
1	20 min	99%	495	10	30 min	96%	4845
2	20 min	98%	985	11	40 min	95%	5320
3	20 min	99%	1480	12	50 min	96%	5800
4	20 min	97%	1965	13	1 h	95%	6275
5	20 min	96%	2445	14	1.5 h	95%	6750
6	20 min	95%	2920	15	3 h	97%	7235
7	30 min	95%	3395	16	9 h	97%	7720
8	30 min	98%	3885	17	24 h	94%	8190
9	30 min	96%	4365				

[a] Reactions performed at 75 °C under N_2 atmosphere using 2 mmol of substrate (1 M solution in glycerol). [enynol : Pd] ratio = 500 : 1. [b] Determined by GC. [c] Cumulative TON values.

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yellow solid precipitate was then filtered, washed twice with methanol (5 cm^3), and dried *in vacuo*. Yield: 109 mg, 84% (Found: C, 41.82; H, 5.33; N, 11.40%. $C_{26}H_{38}Cl_4N_6P_2Pd$ requires C, 41.93; H, 5.24; N, 11.28%). Conductivity (water, 20 °C) 207 Ω^{-1}cm^2 mol^{-1}. δ_P(DMSO-d_6) -16.98 (s); δ_H(DMSO-d_6) 4.35–4.44 (m, 12H, PCH$_2$N), 4.74–4.87 (m, 12H, NCH$_2$N), 5.33 (br, 4H, NCH_2Ph), 7.50–7.55 (m, 10H, Ph);δ_C(DMSO-d_6) 49.9 and 52.3 (br, PCH$_2$N), 64.0 (s, NCH$_2$Ph), 68.3 and 78.2 (s, NCH$_2$N), 125.4 (s, C of Ph), 128.8, 130.2 and 132.6 (s, CH of Ph).

16 ***General procedure for the catalytic reactions***: The corresponding (*Z*)-enynol (2 mmol) and the appropriate solvent (2 cm^3) were introduced into a sealed tube under nitrogen atmosphere. Complex *cis*-[PdCl$_2$(DAPTA)$_2$] (2.5 mg, 0.004 mmol; 0.2 mol% of Pd) was then added at room temperature, and the resulting solution heated at 75 °C for the indicated time (the course of the reaction was monitored by regular sampling and analysis by GC). Fractional Kügelrohr distillation of the crude reaction mixtures generated in glycerol provided analytically pure samples of the furans, whose identity was assessed by comparison of their ^{1}H and ^{13}C{^{1}H} NMR data with those previously described in the literature, and by their fragmentation in GC-MS.

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18 Due to its lower solubility in water, small amounts of the catalyst dissolve in the organic phase.

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