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Poly(ethylene glycol) as a Reaction Matrix in Platinum- or Gold-Catalyzed Cycloisomerization: A Mechanistic Investigation

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Transition-metal-catalyzed cycloisomerization has recently become a fundamental chemical transformation for the synthesis of a large variety of organic molecules including heterocycles.^[1] Usually, the reaction is performed under homogeneous conditions: a starting material is stirred in an organic solvent with a metallic salt, often under conventional heating in an oil bath. Treatment of the reaction including aqueous work-up, followed by purification by silica gel chromatography, provides the expected product. These reactions are carried out with noble-metal-based catalysts such as platinum^[1i,j,m,2] and gold,^[1i,k,m,2,3] which are becoming rare and expensive. So far, efforts to recover and recycle these salts in the frame of these transformations have been scarce.^[4] Furthermore most of these reactions are carried out in "classical" organic solvents, often volatile, toxic and detrimental to the environment, whereas solvent-consuming purification methods are required, with the formation of waste. Herein, we report on an alternative and new highly efficient catalytic system for the cycloisomerization of alkynyl diols and amino alcohols to provide furan and pyrrole derivatives^[4f,5] based on late carbophilic transition-metals such as platinum or gold mixed in eco-friendly poly(ethylene glycol) matrix (PEG), under microwave activation. The elaboration of this system was based on the postulate that the presence of PEG would stabilize and encapsulate metallic species, preventing aggregation and deactivation. PEG could also play the role of solvent^[6] when used at a temperature above its melting point, efficiently heated by microwaves, thus providing a safe reaction environment. Finally, recovery of the product and the catalytic system was performed by a simple, fast, and effective precipitation/filtration work-up to provide the pure product after evaporation of the filtrate and the catalytic system as PEG-based solid.^[7] The results presented herein confirm the validity of this approach. We report unprecedented results with platinum and gold catalysts, by studying the efficiency of the PEG-based catalytic system, its recycling, its improvement by using an oxidant, and provide an insight into the nature of the metal-

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lic species in the PEG matrix. These new systems compare favorably to other catalytic systems in terms of efficiency and handling of the work-up procedure.

The hydroxyalkoxylation was studied in which the Pt or Au catalyst is activating an alkyne towards nucleophilic attack by an oxygen or nitrogen atom. The reaction of alkynyl diol 1a was used as a test reaction to explore various catalysts that could catalyze the 5-endo-dig cycloisomerization to afford furan 2a when embedded in the PEG 3400matrix (Table 1). Temperatures higher than 55°C (corresponding to the melting point of PEG-3400) were used. Since microwave heating is focused on the reaction mixture and because PEG polymers are effective microwave absorbers, this technique is practical because it ensures the rapid melting of the polymer during the reaction. In a typical experiment, compound **1a**, a transition-metal salt (2 mol%), and PEG-3400 were charged in a microwave vessel and heated under microwave irradiation above 50°C for 15-60 min. At the end of the allotted time, the mixture was di-

Table 1. Screening of reaction conditions for the cycloisomerization of **1a**. $[\mathbf{D}_{\mathbf{1}}]_{\mathbf{2}} = [\mathbf{1}, \mathbf{1}]_{\mathbf{2}} = [\mathbf{1}, \mathbf{2}]_{\mathbf{2}} = [\mathbf{1},$

	Ph [Pt] or [Au] (2 mol %) Ph				
	HO Ph	PEG-3400	_		
	ОН Г	Microwaves	-	^C O ^{Ph}	
	1a			2a	
Entry	Catalyst/Additive ^[a]	Т	t	Yield	
	-	[°C]	[min]	[%] ^[b,c]	
1	AuCl(PPh ₃)	50	60	5 (30)	
2	AuCl(PPh ₃)/AgOTf	50	60	50 (100)	
3	AuCl(PPh3)/AgSbF6	50	60	54 (100)	
4	AuCl(PPh3)/AgSbF6	50	15	81 (100)	
5	AuCl(PPh3)/AgSbF6	50	15	98 ^[d] (100)	
6	AuCl ₃	50	15	60 (80)	
7	AuCl ₃	50	60	53 (100)	
8	AuCl ₃ /AgOTf	50	60	52 (100)	
9	AuCl ₃ /AgSbF ₆	50	60	52 (100)	
10	AuCl ₃	50	30	85 (100)	
11	AuCl ₃	50	30	79 ^[d] (100)	
12	PtCl ₂	50	15	$0^{[d]}(0)$	
13	PtCl ₂	50	30	15 ^[d] (15)	
14	PtCl ₂	80	15	70 (100)	
15	PtCl ₂	80	30	80 (100)	
16	PtCl ₂	80	30	83 ^[d] (100)	

[a] Typically: compound **1a** (0.13 mmol), PEG-3400 (300 mg), catalyst/additive (2 mol %, 1:1 for Au¹ and 1:3 for Au^{III}). [b] Yields were determined by ¹H NMR spectroscopic analysis versus internal standard. [c] HPLC conversion is given in parenthesis. [d] Cooling option was used during microwave irradiation.

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luted with a small amount of CH2Cl2, precipitated in Et2O and filtered. The filtrate was concentrated in vacuo and analyzed by ¹H NMR spectroscopy with an internal standard. Gold and platinum salts were tested in this reaction and the results obtained are presented in Table 1. AuCl(PPh₃) was first tested at 50°C for 1 h (Table 1, entry 1) but provided low conversion and product yield. Full conversion of substrate was possible by addition of a silver salt (AgOTf or AgSbF₆), providing a more efficient activation of the substrate through the formation of a more electrophilic cationic gold(I) species by ligand exchange (Table 1, entries 2 and 3). However, the expected product was still obtained in moderate yield, probably due to a long reaction time, which caused its degradation. Adding AgSbF₆ and reducing the reaction time to 15 min maintained the full conversion and improved the yield dramatically (Table 1, entry 4). Silver catalvsis was excluded after performing a control experiment in the absence of gold(I): the final product was obtained in traces and extensive substrate degradation was observed. By using the same reaction conditions $(AuCl(PPh_3)/AgSbF_6)$ under microwave irradiation with a simultaneous cooling system, a quantitative yield of furan 2a was obtained (Table 1, entry 5). This technique provided sufficient heating for the reaction to occur without producing concomitant degradation. A similar study was performed with AuCl₃ but 15 min was too short a reaction time (Table 1, entry 6); extending to one hour provided full conversion but with a moderate yield (Table 1, entry 7) even in the presence of silver additives (entries 8 and 9). Finally, furan 2a was obtained in a good yield by reducing the reaction time to 30 min, with or without the cooling technique (Table 1, entries 10 and 11). PtCl₂, which to our knowledge was never used in this cycloisomerization, was also tested. Temperature adjustment with respect to gold-catalyzed processes was necessary: at 50 °C (Table 1, entry 12) the reaction did not proceed after 15 min, whereas only 15% of conversion was obtained after 30 min (entry 13). A higher temperature (80°C), compound 2a was obtained in a very good yield after only 30 min (Table 1, entries 15 and 16). Reactions performed in the absence of catalyst, that is, in the presence of AgSbF₆ or TfOH only, did not yield any product. To delineate the scope of the reaction, various alkynyl diols were prepared and cyclized with the three catalytic systems explored on the model reaction (Figure 1). Generally, a reaction time of only 15-30 min was needed to complete the reaction. Various substituents could be accepted on the starting material.

It is noteworthy that a monosubstituted furan (2e), in some cases difficult to isolate and purify,^[5c,h] could be effectively prepared by this method starting from a molecule bearing an unsubstituted alkyne; in addition, no hydration of the unsubstituted alkyne was observed in this case. The reaction proved to be general with the different catalysts. In all cases, the conversions were complete and the yields were very good to excellent, or very often quantitative. The precipitation/filtration procedure was performed and afforded the expected product with an excellent purity (>99% by



Figure 1. Yields of the isolated substituted furans by cycloisomerization in PEG/metal/MW conditions.

HPLC) and did not require further purification such as recrystallization or column chromatography. Both metals, Au and Pt were very satisfying in this cycloisomerization, especially when PEG-3400 was heated by microwave irradiation. The synthesis of furane 2b was also explored under the same reaction conditions developed for each PEG/metal catalytic system, but by heating up with an oil bath. Full conversion of substrate could be obtained only for PEG/Pt^{II} catalytic system, but the final product was obtained in lower yield (81%). In the case of the catalytic system PEG/Au¹/ Ag^I, incomplete conversion of **1b** led to **2b** in a lower yield (80%). In the case of PEG/Au^{III} system, heating by using an oil-bath was detrimental, and compound 2b could not be obtained because of extensive degradation of the substrate. Compared with other catalytic systems and procedures,^[5] the present process, activated by microwave irradiation, represents a very practical, efficient, and fast access to furans, especially with the Au^{III} catalyst, which is more efficient in terms of product yields and metal-loading.

By using these general conditions, a similar transformation, heterocyclization of alkynylamino alcohols into pyrroles, was also performed. Di- and trisubstituted pyrroles **4a-e** were obtained from linear substrates **3a-e** in good to excellent yields, after separation by filtration from the PEGcatalytic system, because the conversions were always complete (Scheme 1). Next, we investigated the nature of the electrophilic catalytic system and its recycling ability. Recycling was tested on the transformation of diol **1b** in furan **2b**. After the precipitation/filtration step, which provided furan **2b**, the recovered solid consisting of PEG and metal catalyst was used again in another cycloisomerization of **1b**. This procedure was repeated successively until the catalytic activity dropped, resulting in an incomplete conversion. This assay was performed with the three different metallic sys-

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Scheme 1. Synthesis of substituted furans by cycloisomerization.

tems used in this study and the results are presented in Figure 2. The Pt-catalyzed cycloisomerization was performed four times without a loss of catalytic activity, each time resulting in a complete conversion and a very good yield ranging from 82 to 92%. This was not the case for the AuCl(PPh₃)/AgSbF₆ or AuCl₃ systems, which could be used



Figure 2. Recycling experiments of PEG/metal system and oxidative modified conditions. Bottom: purple PEG/PtII; yellow PEG/Au^{II}/Ag^I; white PEG/Au^{III}; red PEG/Au^{III}+5.

only twice before losing their activity. One possible explanation for the decrease of activity could be the degradation of the catalyst into various homogeneous species and their loss during the precipitation/filtration process. This was evaluated by performing inductively coupled plasma-mass spectrometry (ICP-MS) analyses of the organic product obtained in the filtrate after each run. In the case of platinum, 22% of the initial amount of catalyst was lost after one run. A further 11% was lost in the next run, whereas after four runs, about half of the catalyst was retained in the polymer matrix. However, even if the amount of catalyst decreased dramatically, the catalytic activity remained high for each of these four cycles. In sharp contrast, the amount of catalyst recovered in the PEG matrix for Au^{III} or Au^{III} salts was much higher since in each cycle less than 1% of the initial quantity catalyst was lost. This probably arises from the oxophilicity of gold, which generates strong metal-polymer interactions. Nevertheless, the catalytic activity dropped dramatically after two runs. Even if the quantity of catalyst retained in the PEG matrix is the major factor that governs the efficient recycling, another crucial parameter is the oxidation state of the metal. The cycloisomerization described herein is considered to occur through π -bond activation by ionic complexes^[4e] (Pt²⁺, Au¹⁺, or Au³⁺). Microwave irradiation of a mixture of AuCl₃ (or PtCl₂) in the presence of PEG resulted in the formation of PEG-stabilized nanoparticles of Au (or Pt, respectively), as confirmed by performing spectroscopic studies such as transmission electronic microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). These spherical particles have even, narrow size-distribution, and arose from the reduction of PtCl₂ (ca. 5–7 nm)^[8] or AuCl₃ (and ca. 3-5 nm), with PEG under microwave activation, similar to the polyol method^[9] used to generate such species.^[10] This was further confirmed by XPS analysis of the samples of catalytic systems, which detected a mixture of M^0 (M=Pt, Au) and M^{n+} (n=2, 3, respectively), the major metallic species being the reduced metal, resulting in a deactivation of the catalyst.^[8,11] The catalytic cycle describing this situation in the case of gold^[12] is depicted in Scheme 2.

Figure 3 presents the XPS spectrum of gold nanoparticles after the first run followed by a precipitation/filtration work-up. After deconvolution, the Au 4f spectrum is observed presenting a doublet signal centered on 87.84 and 84.20 eV, respectively, corresponding to the Au $4f_{7/2}$ and



Scheme 2. Redox competitive pathways in gold-catalyzed cyclizations.

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Figure 3. XPS spectrum of the PEG/AuCl₃ catalytic system after precipitation/filtration work-up.

Au $4f_{5/2}$ spin-orbit components and satisfying the characteristic separation of the Au 4f (3.6 eV) of Au^{0[13]} (Figure 3).

This confirms the generation of inactive metallic species during the course of the cyclization. Because of the better retention of gold by the polymer matrix, we focused our attention to the study of this metal. To overcome the reduction problem, an oxidant, which could bring back the oxidation state of Au from 0 to +3 (or another higher oxidation state), was used concomitantly to activate the catalytic cycle again and produce the organic molecule.^[4e,14] Initial results obtained by XPS analysis of the platinum catalyst^[12] showed that oxidants such as benzoquinone **5**, PhICl₂, and PhI-(OAc)₂, could bring the oxidation state of Pt⁰ (after the first reaction) back to +2.^[4e,12]

Worth noticing is the use of an oxidation method in which stoichiometric quantities of heavy and toxic metals are avoided. We investigated the structural validity of this approach by XPS analysis of the most efficient catalyst based on gold, AuCl₃, in the presence of benzoquinone **5** and PEG after reaction and precipitation/filtration (Figure 2). The oxidant was employed in a catalytic amount (3 catalytic equivalents, which corresponds to 6 mol%). Despite its high oxidation potential, Au⁰ could be efficiently reoxidized to a catalytically active species. The complete disappearance of the Au⁰ species and the exclusive formation of Au¹ species with two signals at 84.52 eV (Au 4f_{7/2}) and 88.18 eV (Au 4f_{5/2})^[13] is demonstrated by XPS spectra through a shift of the doublet to a higher binding energy.

This can be clearly seen on the comparative spectra in Figure 4. With the exception of palladium,^[14] XPS insight on the catalytic behavior of PEG-stabilized nanoparticles have never been reported so far. The Au⁰ nanoparticles were not transformed back to the Au +3 complexes but to Au +1, species which are electrophilic enough to carry out the cyclization efficiently. This correlates with the excellent results obtained in recycling the catalytic system initially made of AuCl₃ benzoquinone, and PEG. The catalytic system was recycled five times without appreciable loss of activity, whereas only one recycle was possible working in the absence of oxidant (Figure 2).



Figure 4. XPS spectrum of the PEG/Au⁰ catalytic system after recycling in the presence of oxidant **5**.

In summary, we have designed a new catalytic system made of PEG and a transition metal (Pt or Au) and illustrated its efficiency in the cycloisomerization of alkynyl diols and amino alcohols under microwave irradiation. The cyclization is very effective with all the substrates and catalysts tested. The heterocycles thus obtained can be efficiently separated from the reaction mixture by a precipitation/filtration technique and obtained with a high purity without purification by column chromatography. In the case of gold, the electrophilicity of the nanoparticle catalytic system can be maintained by adding a catalytic amount of an oxidant such as benzoquinone. This resulted in the successful recycling of the catalytic system in five consecutive runs.

Experimental Section

A typical experimental procedure for the heterocyclization of 1,2-diols: Substrate 1b (28.3 mg, 0.13 mmol) was added to a mixture of AuCl₃ (0.0026 mmol) and PEG-3400 (300 mg). The resulting mixture was heated by using microwave irradiation at 50 °C (initial power 400 W and cooling ON) for 15 min. The reaction mixture was solubilized in CH₂Cl₂ (1.5 or 2.0 mL) and was added slowly at RT to Et₂O (150 mL) for precipitation. After 3 h at -18°C, filtration of PEG-3400/catalyst and evaporation of ether afforded 2-butyl-4-phenyl-furan (2b) (24.2 mg, 93%) as a pure oil. ¹H NMR (CDCl₃, 300 MHz): $\delta = 7.51$ (s,1 H), 7.40–7.37 (m, 2 H), 7.27-7.25 (m, 2H), 7.18-7.13 (m, 1H), 6.23 (s, 1H), 2.58 (t, 2H, J= 7.7 Hz), 1.61–1.54 (m, 2H), 1.34–1.27 (m, 2H), 0.87 ppm (t, 3H, J= 7.3 Hz);¹³C NMR (CDCl₃, 75 MHz): $\delta = 157.8$, 136.6, 133.0, 128.8, 127.6, 127.0, 126.7, 125.7, 104.0, 30.1, 27.9, 22.3, 13.9 ppm; IR (neat): $\tilde{\nu} = 2957$, 2930, 2863, 1770, 1601, 1551, 1449, 1128, 928, 739 cm⁻¹; MS (ESI): m/z 201.1 $[M+H]^+$; HMRS (ESI): m/z calcd for $C_{14}H_{17}O$: 201.1253 [*M*+H]⁺; found: 201.1279.

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