## Sol–Gel Immobilized N-Heterocyclic Carbene Gold Complex as a Recyclable Catalyst for the Rearrangement of Allylic Esters and the Cycloisomerization of γ-Alkynoic Acids

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Dedicated to the memory of Professor Robert J. P. Corriu

The synthesis of a bis-silylated (NHC)AuCl (NHC=N-heterocyclic carbene) complex and the formation of a hybrid silica material by the sol-gel process by cogelification with tetraethylorthosilicate under fluoride catalysis are described. This material was characterized by using <sup>29</sup>Si solid-state NMR spectroscopy, N<sub>2</sub> sorption measurements, electron microscopy, and elemental analysis. It was tested as a reusable catalyst in the rearrangement of allylic esters in conjunction with a silver salt under microwave conditions and it displayed a much better performance than a homogeneous analogue. This catalyst is active and recyclable in the cycloisomerization of  $\gamma$ -alkynoic acids to five-membered enol-lactones at room temperature in two reaction media, a toluene/water biphasic system and a deep eutectic solvent.

### Introduction

 $\mathsf{Au}^{\text{I}}$  and  $\mathsf{Au}^{\text{III}}$  species have gained an increasing popularity in homogeneous catalysis<sup>[1]</sup> because of their excellent  $\pi$ -coordinating properties, which allow the activation of unsaturated substrates, such as alkynes,<sup>[2]</sup> alkenes,<sup>[3]</sup> and allenes,<sup>[4]</sup> towards the addition of a wide variety of nucleophiles. The stability, reactivity, and selectivity of Au catalysts can be fine-tuned by the proper choice of ancillary ligands. In this sense, N-heterocyclic carbenes (NHC) combine strong  $\sigma$ -donating properties with a steric profile that leads to both the electronic and steric stabilization of the metal center and enhancement of its activity. which lead to significant advantages over classical complexes that bear phosphine or phosphite ligands.<sup>[5]</sup> NHC-Au catalysis encompasses a wide variety of organic transformations such as skeletal rearrangements, cycloisomerizations, the addition of water to alkynes and nitriles, and C-H bond activation.[5-7] In particular, (NHC)AuCl complexes have been involved in the catalytic cycloisomerization of  $\gamma$ -alkynoic acids into enol-lactones [8,9] and, in conjunction with a silver salt, in the

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rearrangement of allylic acetates.<sup>[10]</sup> In addition, they have been decisive for the systematic isolation of vinyl- and aryl-gold(I) intermediates in catalytic cycles.<sup>[11]</sup>

However, homogeneous catalysts present several drawbacks such as deactivation through decomposition pathways and difficult recycling, which can be overcome by heterogenization. To the best of our knowledge, very few examples of immobilized (NHC)Au<sup>1</sup> catalysts have been reported. (NHC)AuCl complexes supported on porous organic polymers (POP) have been used as heterogeneous catalysts for alkyne hydration.<sup>[12]</sup> Corma et al. have described the grafting of a (NHC)AuCl complex onto mesoporous silica MCM-41 and zeolite ITQ-2 for the hydrogenation of diethyl citraconate.<sup>[13]</sup> Several (NHC)-dioxolane Au<sup>1</sup> complexes grafted to MCM-41 have been reported as reusable catalysts in a three-component coupling reaction of aldehydes, amines, and terminal alkynes to afford propargylamines.<sup>[14]</sup>

Following our studies on NHC-Pd,<sup>[15]</sup> NHC-Ru,<sup>[16]</sup> and NHC-Rh,<sup>[17]</sup> recyclable catalysts prepared by sol-gel methodologies,<sup>[18]</sup> we present herein our results on the synthesis of a silica-supported (NHC)AuCl catalyst obtained by a sol-gel procedure from a silylated NHC-gold(I) precursor and its activity and reusability in the rearrangement of allylic esters and the cycloisomerization of  $\gamma$ -alkynoic acids.

### **Results and Discussion**

The synthesis of the bis-silylated (NHC)AuCl precursor **3** was undertaken as summarized in Scheme 1. *meso*-Diallyl dihydroimidazolium chloride (**1**)<sup>[16b, 17]</sup> was treated with silver oxide in dichloromethane at room temperature. Further transmetallation of the corresponding [NHC-Ag<sup>I</sup>] species in the presence of



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Scheme 1. Synthesis of the bis-silylated Au<sup>l</sup> complex 3.

an equivalent of chloro(dimethyl sulfide)gold(I)<sup>[19]</sup> in dichloromethane at room temperature, afforded the gold(I) complex **2** in 88% yield after chromatographic purification. Hydrosilylation with trichlorosilane in the presence of the Karstedt catalyst followed by treatment with ethanol/triethylamine afforded **3** in 26% isolated yield.

To improve the overall yield of **3** an alternative synthesis was attempted, namely, through a free carbene route from the bis-silylated dihydroimidazolium chloride **4** obtained from **1** as described previously<sup>[16b]</sup> (Scheme 2).

Although the treatment of **4** with chloro(dimethylsulfide)gold(I) in acetone at 60 °C<sup>[20]</sup> or chloro(tetrahydrothiophene)gold(I) in dichloromethane at room temperature<sup>[21]</sup> allowed the formation of **3** in respectable 69 and 72% yields (after the filtration of the crude mixture through Celite) on small scale (0.1 mmol), the reactions failed if they were scaled up to 0.3 mmol. Moreover, the solid obtained in the second case decomposed and turned from white to black after two days. The transmetallation route from the silylated salt **4** was also unsuccessful and led to decomposition and the formation of a pinkish solution. Notably, in our hands, the syntheses of the analogous NHC complexes of Ru<sup>[16b]</sup> and Rh<sup>[17]</sup> from the bis-silylated salt **4** were successful. The organosilica **M1** was prepared from **3** by cogelification with tetraethyl orthosilicate (TEOS; **3**/TEOS molar ratio of 1:30). The reaction was performed under Ar in anhydrous and degassed DMF at room temperature using a stoichiometric amount of water (with respect to the ethoxy groups) and tetrabutylammonium fluoride as a nucleophilic catalyst (1 mol% with respect to Si; Scheme 3). The solution gelified after 30 min and was aged for six days at room temperature under Ar. Then, the solid was collected by filtration and washed successively with dry and degassed ethanol, acetone, and diethyl ether. Residual DMF entrapped in the material was removed by Soxhlet extraction with dry and degassed chloroform. The resulting white powder was dried overnight at 40 °C under vacuum.

This material was characterized by <sup>29</sup>Si solid-state NMR spectroscopy, N<sub>2</sub> adsorption–desorption measurements, TEM, SEM, energy-dispersive X-ray spectroscopy (EDX), and elemental analysis. The <sup>29</sup>Si cross-polarization magic-angle spinning (CP-MAS) NMR spectrum of **M1** (Supporting Information) confirmed the covalent bonding of the organic moiety to the silica matrix by the presence of a T<sup>3</sup> signal (C–SiO<sub>3</sub> environments) at  $\delta = -66.0$  ppm in addition to the characteristic Q<sup>3</sup> and Q<sup>4</sup> signals that correspond to the condensed TEOS at  $\delta = -104.0$ 



Conditions a: [Au(SMe<sub>2</sub>)Cl], K<sub>2</sub>CO<sub>3</sub>, acetone (anh.), 60 °C, Ar atm, (69% yield, scale: 0.1 mmol) Conditions b: [Au(THT)Cl], K<sub>2</sub>CO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> (anh.), rt, Ar atm, (72% yield, scale: 0.1 mmol)

Scheme 2. Alternative synthesis of the bis-silylated Au<sup>1</sup> complex 3.



Scheme 3. Synthesis of hybrid silica material M1.

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and -110.0 ppm, respectively. The high dilution of the organic moiety in the inorganic matrix precluded the observation of the corresponding signals in the <sup>13</sup>C solid-state NMR and IR spectra.

As observed by TEM (Figure 1), the material is formed as an agglomerate of primary nanoparticles (50–100 nm). This should enable the easy diffusion of the reaction mixtures within the material through the interstices. Furthermore, an important mesoporosity (total pore volume  $0.62 \text{ cm}^3 \text{g}^{-1}$  and BET surface



Figure 1. TEM image of hybrid silica material M1. Scale bar = 500 nm.

area 818 m<sup>2</sup>g<sup>-1</sup>) is present within the particles, as deduced from N<sub>2</sub> sorption experiments (Figure 2). The isotherm is of Type IV, representative of a mesoporous material with a sharp pore diameter distribution centered at 35 Å. Notably, there is no noticeable microporosity, as deduced from the *t*-plot. The Au content was determined by inductively coupled plasma optic emission spectroscopy (ICP-OES) analysis (2.99% w/w, 0.15 mmol Au/g material). As the elemental analysis revealed an Au/Si ratio of 1:66 and the theoretical value should be 1:32 (if we assume complete condensation), it is likely that incomplete condensation and the partial loss of the metal occur

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Scheme 4. Rearrangement of allylic esters under Au<sup>l</sup> catalysis.

during the formation of the material by the sol-gel process. It should be emphasized that the material is a white solid (Figure S1) and neither TEM nor SEM showed clear evidence of the presence of Au nanoparticles that would result from the partial decomposition of the precursor **3** during the sol-gel process.

First, as a model and for comparison, the homogeneous Au<sup>1</sup> complex 2 (3 mol%) was tested in the allylic isomerizations of ester 5a in conjunction with a silver salt (2 mol% of AgBF<sub>4</sub>) in 1,2-dichloroethane (DCE) (Scheme 4 and Table 1). As a very low conversion was achieved with 2 as the catalyst after 2 days of the reaction of 5a in 1,2-dichloroethane heated to reflux, two experiments with this homogeneous catalyst were performed under microwave heating (200 W, 80 °C; Table 1, entries 1 and 2). Although the complete conversion was observed by <sup>1</sup>H NMR spectroscopy, the isolated yields of **6a** were only 17 and 15% at 30 and 12 min of reaction, respectively, because of extensive oligomerization. Strikingly, under the same microwave conditions, the desired product **6a** was obtained in 93% yield after 40 min by using the supported Au complex M1, without the formation of any byproducts (Table 1, entry 3, cycle 1). Moreover, the reusability of the catalyst was demonstrated, and two more runs could be performed with



Figure 2. N<sub>2</sub>-sorption isotherm of M1. Inset: pore size distribution (BJH on desorption branch).

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Table 1. Rearrangement of allylic esters catalyzed by Au <sup>1</sup> .				
Entry <sup>[a]</sup>	Cat/ <b>5</b>	Cycle	<i>t</i> [min]	<b>6</b> [%] <sup>[b]</sup>
1	2/5 a	1	30	<b>6a</b> (17)
2	2/5 a	1	12	<b>6a</b> (15)
3	M1/5 a	1	40	<b>6a</b> (93)
4	M1/5 a	2	40	<b>6a</b> (94)
5	M1/5 a	3	40	<b>6a</b> (83)
6	M1/5 b	1	40	<b>6b</b> (83)
7	M1/5 b	2	40	<b>6b</b> (79)
8	M1/5 b	3	40	<b>6b</b> (71)
9	M1/5 c	1	40	<b>6c</b> (71)
10	M1/5 c	2	40	<b>6c</b> (72)
11	M1/5 c	3	40	<b>6c</b> (59)
12	M1/5 d	1	75	<b>6 d</b> (69)
13	M1/5 d	2	60	6d (74)
14	M1/5 d	3	60	6d (74)
15	M1/5 e	1	40	<b>6e</b> (40)
16	M1/5 e	2	40	<b>6e</b> (57)
[a] 80 $^\circ\text{C}$ under microwave activation (200 W maximum), 0.25 mmol of <b>5</b> in 0.6 mL 1,2-dichloroethane. [b] Isolated yield.				

the same batch of catalyst recovered by filtration (Table 1, entries 4 and 5, cycles 2 and 3). Other secondary allylic acetates **5b-c** (Table 1, entries 6–8 and 9–11), secondary allylic benzoate **5d** (Table 1, entries 12–14), and tertiary allylic acetate **5e** (Table 1, entries 15–16) were also isomerized successfully using **M1** under microwave conditions, and the catalyst was recycled in each case. The benzoate **5d** required longer reaction times.

The need for a Ag salt as the chloride abstractor to generate the true catalytic species  $[(NHC)Au]^+$  has been avoided in the cycloisomerization of  $\gamma$ -alkynoic acids catalyzed by water-soluble (NHC)AuCl complexes in a water/toluene biphasic system.<sup>[8a]</sup> The presence of water facilitates the liberation of the chloride ligand. This prompted us to assay our supported catalyst **M1** in this process under these conditions. In a first set of experiments, we tested the homogeneous catalyst **2** and **M1** (2.5 mol%) in the cycloisomerization of 4-pentynoic acid (**7***a*; [**7***a*]=0.15 M) to the lactone **8***a* in a 1:1 water/toluene mixture at room temperature (Scheme 5). Whereas **2** led to an isolated



Scheme 5. Cycloisomerization of 4-pentynoic acid under Au<sup>1</sup> catalysis.

80% yield of **8a** after 4 h, no conversion was achieved with **M1** after 18 h under magnetic stirring, and the material became pinkish. At this point, we thought that the type of stirring could be crucial for the evolution of the reaction and we changed the magnetic stirrer to a wrist-type shaker (rocking mixer vibromatic). This enables the good mixing of the immiscible layers, and the insoluble **M1**, which remains at the

interphase, can be in contact with both water and toluene. To our delight, after 2 days, a complete conversion was observed, and **8a** was isolated in 75% yield. Moreover, the catalyst **M1** could be recycled successfully in up to six runs and suffered no damage to remain as a white solid. In all cases, the conversion was complete and good isolated yields of **8a** were obtained (Scheme 5).

Encouraged by these results, other alkynoic acids 7 b-d were subjected to the reaction with M1 under the same conditions (Scheme 6).



Scheme 6. Cycloisomerization of 7b-d catalyzed by M1 in water/toluene.

Compounds **7b** and **7c**, which bear two and one terminal alkyne units, respectively, afforded the five-membered enol-lactones **8b** and **8c** selectively. Furthermore, **M1** was recycled in both cases. By contrast, internal diyne **7d** was transformed into a 4:1 mixture of five- and six-membered enol-lactones **8d** and **8d**' (5-*exo*-dig vs. 6-*endo*-dig)<sup>[8]</sup> in an overall 98% yield. The selectivity decreased upon recycling to a 2:1 mixture in the second run, although no loss of activity was found. In particular, the chemoselectivity offered by the catalyst in this biphasic medium is noteworthy as byproducts derived from alkyne hydration were not observed despite the presence of water.

The use of green and bio-renewable solvents is a lasting challenge. In this sense, deep eutectic solvents (DES) have been used as environmentally friendly solvents in a variety of applications, which include biological transformations, metal processing, the purification of biodiesel, organic synthesis, materials chemistry, and catalytic processes.<sup>[22]</sup> Several advantages, such as low toxicity, high availability, low flammability, high recyclability, low volatility, biodegradability, and low price, make them attractive alternatives for use in academia and industry. DESs are mostly obtained by mixing a low-cost and readily available quaternary ammonium salt (such as choline chloride; ChCl) with a bio-renewable and environmentally benign hydrogen-bond donor (such as glycerol (Gly), lactic acid, urea, or water). Recently, García-Alvarez et al. have reported the cycloisomerization of γ-alkynoic acids in eutectic mixtures of 1 ChCl/  $2\,Urea$  and  $1\,ChCl/2\,Gly$  catalyzed by several Au  $^{\rm l}$  species.  $^{[23]}$ 

Prompted by these precedents, we decided to investigate the use of the mixture of 1ChCl/2Urea as a reaction medium in the cycloisomerization reactions of  $\gamma$ -alkynoic acids **7b-d** 



(0.15 mmol of **7** in 0.150 g of DES) catalyzed by **M1** (2.5 mol%). Complete conversions were achieved, and the reuse of the catalyst in a second run was successful in all cases, but the required reaction times were considerably longer (6 days) than that in the biphasic toluene/water system. The selectivity in the case of **7d** was the same as that attained in the biphasic medium. Remarkably, no loss of selectivity was observed upon recycling, and the preference for the formation of the fivemembered enol-lactone **8d** over **8d**' (4:1) was maintained in the second cycle. Notably, magnetic stirring was suitable for the reactions performed in this medium, and no decomposition of the catalyst occurred.

### Conclusions

A Au<sup>I</sup> complex 3 that bears an N-heterocyclic carbene (NHC) ligand functionalized with two silylated groups was synthesized from the 4,5-diallyldihydroimidazolium salt 1 by a route that involved the formation of (NHC)Ag<sup>l</sup> species, transmetallation to the corresponding (NHC)AuCl complex, and the subsequent hydrosilylation of the two olefinic moieties. The reversal of the order of steps was unsatisfactory. From this precursor, the hybrid silica material M1 was prepared by sol-gel cogelification with tetraethyl orthosilicate under nucleophilic catalysis. This mesoporous material was stable towards air and moisture. M1 was characterized by using standard solid-state techniques, and the Au content was determined by using ICP-OES. This material was evaluated as a recyclable catalyst in two different reactions. It was efficient, in conjunction with a Ag salt, for the rearrangement of allylic esters under microwave activation. Interestingly, M1 exhibited a much better performance than its homogeneous analogue 2. Thus, polymerization byproducts formed under homogeneous conditions were avoided by the use of the silica-supported catalyst, which was reused successfully in up to three runs. Moreover, M1 displayed a good activity in the cycloisomerization of  $\gamma$ -alkynoic acids to enol-lactones in a toluene/water biphasic system at room temperature without the need to add Ag salts. The employment of an appropriate stirring method (wrist-type shaker) was a key factor for the success of the reaction and the preservation of the catalyst, which was reused in up to six cycles. No alkyne hydration byproducts were observed. The activity and recyclability of M1 in the cycloisomerization reaction was also tested successfully in a deep eutectic solvent (1 choline chloride/2 urea) as a green reaction medium at room temperature. To the best of our knowledge, this is the first report of a silica-supported (NHC)Au<sup>l</sup> complex prepared by a sol-gel method from a welldefined silylated NHC-Au precursor, and silica-supported (NHC)Au<sup>l</sup> complexes have not been used previously for the reactions studied here.

### **Experimental Section**

#### **General considerations**

If required, experiments were performed using standard high-vacuum and Schlenk techniques under  $N_{\rm 2}$  or Ar atmosphere using

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dry solvents, which were degassed by the freeze-thaw method and transferred with a cannula or syringe. Commercial reagents were used directly as received except for trichlorosilane, which was purified first by distillation under vacuum and gaseous HCl was eliminated in a second step by performing two freeze-thaw cycles (this compound was always used with a secondary cold trap). Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> used to adsorb water from organic layers were anhydrous. Dry solvents were obtained by using two instruments: PureSolv (Innovative Technologies: THF, CH<sub>2</sub>Cl<sub>2</sub>, and pentane) and in some experiments MBraun SPS-800 (pentane, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, Et<sub>2</sub>O, and toluene). Other dry solvents were prepared using standard methods: CICH<sub>2</sub>CH<sub>2</sub>CI, NEt<sub>3</sub>, and DMF were distilled over CaH<sub>2</sub>. Toluene, benzene, and Et<sub>2</sub>O were heated to reflux with Na/benzophenone, whereas ethanol and methanol were distilled with Mg/I<sub>2</sub>. Acetone was distilled with K<sub>2</sub>CO<sub>3</sub>. If needed, deuterated NMR solvents, such as CDCl<sub>3</sub>, were dried by distillation over CaH<sub>2</sub>. For the preparation of hybrid silica materials, distilled and deionized water was used (MilliQ H<sub>2</sub>O). NMR spectra were recorded at the Servei de Ressonància Magnètica Nuclear of the Universitat Autònoma de Barcelona. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HSQC, <sup>1</sup>H-<sup>13</sup>C HMBC, and selective TOCSY spectra were recorded by using Bruker instruments (DRX-250, DPX-360, and AVANCE-III 400). Chemical shifts ( $\delta$ ) are given in ppm using the residual nondeuterated solvent as the internal reference. <sup>29</sup>Si CP-MAS NMR spectra were recorded at the Université de Montpellier by using a Varian VNMRS 400 MHz instrument. IR spectra were recorded by using a Bruker Tensor 27 spectrometer using a Golden Gate ATR module with a diamond window. Low- and high-resolution mass spectra were obtained by the direct injection of the sample with electrospray techniques by using Hewlett-Packard 5989 A and microTOF-Q instruments, respectively. These analyses were performed by the Servei d'Anàlisi Química (SAQ) of the Universitat Autònoma de Barcelona. Elemental analysis of C, N, H, and Si was performed by the Serveis Científico-Tècnics of the Universitat de Barcelona (SCT-UB). The percentages of C, N, and H were determined by combustion by using an EA-1108 C.E. elemental analyzer from Thermo Scientific with (bis(5-tert-butyl-2-benzoxazol-2-yl) thiophene (BBOT) as the internal standard. The content of Si and Au was determined by ICP-OES by using a multichannel PerkinElmer Optima 3200RL instrument. TLC was performed with 0.25 mm plates (Alugram Sil G/UV<sub>254</sub>). Flash Chromatography was performed under compressed air pressure with Macherey-Nagel GmbH & Co KG silica gel, which had a particle size of 230–400 mesh and a pore volume of  $0.9 \text{ mLg}^{-1}$ . The specific surface area of M1 was determined by the BET method from N<sub>2</sub> adsorption-desorption isotherms obtained by using a Micromeritics ASAP2020 analyzer after degassing samples for 30 h at 55 °C under vacuum. The pore size distribution was determined from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.<sup>[24]</sup> TEM images were obtained by using a JEOL 1200 EX II instrument equipped with a SIS Olympus Quemesa 11 Mpixel camera at the Université de Montpellier. SEM images were obtained at the Institut Européen des Membranes in Montpellier by using a Hitachi S4800 apparatus after Pt metallization. Microwaveassisted reactions were performed by using a CEM Discover® Microwave instrument, which operates between 0 and 300 W (200 W maximum power used). The reactions were conducted in a 10 mL sealed reactor. The temperature was measured by using an IR sensor placed under the reactor. During the experiments compressed N<sub>2</sub> was used to cool the reactor Compounds 1 and 4 were synthesized as reported previously.[16b, 17] Acetates 5a-c and  $e_{,}^{[10]}$  benzoate  $5d_{,}^{[10]}$  diynes 7b and  $d_{,}^{[25]}$  and  $7c^{[26]}$  were prepared following literature procedures. 4-Pentynoic acid (7 a) was supplied by Sigma-Aldrich.



# Preparation of (*meso*-4,5-diallyl-1,3-dimesitylimidazolidin-2-yl)gold(I) chloride (2)

In a Schlenk tube protected from light, a mixture of silver(I) oxide (0.318 g, 1.37 mmol) and 1 (0.983 g, 2.32 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (200 mL) was stirred overnight at RT under Ar. The mixture was filtered through a cannula into another light-protected Schlenk tube, and (dimethylsulfide)gold(I) chloride (0.669 g, 2.27 mmol) was added. The resulting mixture was stirred for 24 h at RT under Ar. Activated carbon was added, and the mixture was filtered through Celite. The filtrates were concentrated under vacuum. The residue was purified by flash chromatography using dichloromethane as the eluent to afford  ${\bf 2}$  as a white solid (1.235 g, 88% yield).  $^1H$  NMR  $(CDCI_3, 400 \text{ MHz}): \delta = 6.92 \text{ (s, 2H. Ar), 6.91 (s, 2H, Ar), 5.47 (m, 2H, 2H, 2H)}$ -CH=), 4.97 (m, 4H, CH2=), 4.42 (m, 2H, CH), 2.62-2.57 (m, 2H, -CH<sub>2</sub>), 2.39 (s, 6H, -CH<sub>3</sub>), 2.36-2.32 (m, 2H, -CH<sub>2</sub>), 2.28 (s, 6H, -CH<sub>3</sub>), 2.27 ppm (s, 6H, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz):  $\delta = 195.2, 139.05, 136.8, 135.5, 133.8, 130.3, 130.25, 118.05, 85.0,$ 31.5, 20.7, 19.06, 17.9 ppm; IR (ATR):  $\tilde{\nu} = 2918$ , 1639, 1610, 1376, 1316, 1260, 1091, 994, 913, 852, 799, 642 cm<sup>-1</sup>; HRMS (ESI): m/z calcd for [<sup>12</sup>C<sub>27</sub>H<sub>34</sub>Au<sup>35</sup>ClN<sub>2</sub>+Na]<sup>+</sup>: 641.1968; found: 641.1974.

#### Preparation of (*meso*-1,3-dimesityl-4,5-bis(3-(triethoxysilyl)propyl)imidazolidin-2-yl)gold(I) chloride (3)

In a sealable Schlenk tube protected from light, 2 (0.961 g, 1.55 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) under Ar. To this solution, freshly distilled  $HSiCl_3$  (3.2 mL, 1.34 g mL<sup>-1</sup>, 31.6 mmol) and Karstedt's catalyst (1.0 mL of a solution of 2 wt% Pt in xylene,  $0.855 \text{ g mL}^{-1}$ , 0.08 mmol Pt) were added. The reaction mixture was stirred under Ar at 40 °C for 3 h. After this time, excess HSiCl<sub>3</sub> was removed by distillation and collected in a secondary cold trap. The residue was redissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and the mixture was cooled to 0°C with an ice bath. Then, anhydrous EtOH/NEt<sub>3</sub> (1:1, 12 mL) was added slowly, and the mixture was stirred at RT for 2 h. The volatiles were removed under vacuum, and the residue was treated with dry toluene and filtered to separate the ammonium salt. The filtrates were concentrated under vacuum, and the resulting brown solid was digested with dry pentane (3×20 mL) and filtered through a cannula each time to another Schlenk tube. The filtrates were concentrated under vacuum to afford 3 as a white solid (0.386 g, 26% yield). The product was stored under Ar and protected from light at RT. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.92$  (s, 2H, Ar), 6.90 (s, 2H, Ar), 4.25 (m, 2H, CH), 3.71 (q, 12H, J=6.9 Hz, -CH<sub>2</sub>), 2.39 (s, 6H, -CH<sub>3</sub>), 2.28 (s, 12H, -CH<sub>3</sub>), 1.79 (m, 2H, -CH<sub>2</sub>), 1.63 (m, 2H, -CH<sub>2</sub>), 1.27 (m, 4H, -CH<sub>2</sub>), 1.17 (t, 18H, J=6.9 Hz, -CH<sub>3</sub>), 0.51 ppm (m, 4H, -CH<sub>2</sub>Si); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz):  $\delta = 194.8$ , 138.7, 136.9, 135.4, 134.9, 130.25, 130.2, 65.25, 58.2, 31.65, 30.7, 29.4, 26.8, 20.7, 20.45, 18.95, 17.97, 17.88, 10.35 ppm; IR (ATR):  $\tilde{\nu} = 2963$ , 2923, 1482, 1389, 1259, 1166, 1075, 1022, 954, 793 cm<sup>-1</sup>; HRMS (ESI): m/z calcd for  $[{}^{12}C_{39}H_{66}Au^{35}CIN_2O_6Si_2+Na]^+$ : 969.3706; found: 969.3706.

#### Preparation of supported gold(I) catalyst M1 by sol-gel cogelification

A solution of **3** (0.772 g, 0.815 mmol) and TEOS (5.5 mL, 0.94 g mL<sup>-1</sup>, 24.8 mmol) in dry and degassed DMF (20 mL) was prepared in a round-bottomed Schlenk flask under Ar. Under stirring, a solution of tetrabutylammonium fluoride (TBAF) (0.26 mL, commercial solution 1  $\mu$  in anhydrous THF, 0.26 mmol, 1 mol% F with respect to Si) and MilliQ water (1.9 mL, 105 mmol, H<sub>2</sub>O/EtO = 1) in dry and degassed DMF (5 mL) was added to the first solution. The

mixture was stirred at RT for 15 min, then the stirring was stopped. A gel formed within 20 min and was left to age at RT under Ar and protected from light for 6 days. At this time, the gel was pulverized, filtered, washed through a cannula with dry and degassed EtOH (3×15 mL), dry and degassed acetone (3×15 mL), and dry and degassed diethyl ether (3×15 mL). Then the solid was washed with dry and degassed CHCl<sub>3</sub> in a Soxhlet apparatus for 48 h to remove the residual DMF entrapped in the material. After drying overnight at 40 °C under vacuum, **M1** was obtained (1.419 g) as a white solid. <sup>29</sup>Si-CP-MAS NMR (79.5 MHz):  $\delta = -66.0$  (T<sup>3</sup>), -104.0 (Q<sup>3</sup>), -110.0 ppm (Q<sup>4</sup>); BET  $S_{BET}$ : 818 m<sup>2</sup>g<sup>-1</sup>; pore diameter distribution centered around 35 Å; pore volume: 0.62 cm<sup>3</sup>/g; elemental analysis: calcd (%) for C<sub>27</sub>H<sub>36</sub>N<sub>2</sub>ClAuSi<sub>32</sub>O<sub>63</sub> (which assumes complete condensation): C 12.8, H 1.44, N 1.11, Au 7.80, Si 35.4; found: C 17.72, H 2.91, N 1.06, Au 2.99, Si 28.0 (0.15 mmol<sub>[(NHC)Au]</sub>g<sub>M1</sub><sup>-1</sup>).

#### Procedure for the rearrangement of allylic acetate 5 a catalyzed by 2

AgBF<sub>4</sub> (3.9 mg, 0.02 mmol, 2 mol%) was added to a dry 1,2-dichloroethane (DCE) solution (1.7 mL) of **2** (0.019 g, 0.03 mmol, 3 mol%) in a microwave vial under protection from light and an inert atmosphere. The solution became cloudy instantly, and the mixture was stirred for 1 min before a dry DCE solution (0.6 mL) of the allylic ester (1 mmol, 1 equiv.) was added. The vial was then placed in a microwave reactor and heated at 80 °C for the time indicated in Table 1. The resulting mixture was dissolved in pentane, filtered through Celite, and the solvent from the filtrate was evaporated. The crude product **6a** was purified by flash chromatography on silica gel.

# General procedure for the rearrangement of allylic esters catalyzed by M1

AgBF<sub>4</sub> (3.9 mg, 0.02 mmol, 2 mol%) was added to a dry DCE solution (1.7 mL) of **M1** (0.197 g, 0.03 mmol, 3 mol%) in a microwave vial under protection from light and an inert atmosphere. The mixture was stirred for 1 min before a dry DCE solution (0.6 mL) of the corresponding allylic ester **5** (1 mmol, 1 equiv.) was added. The vial was then placed in a microwave reactor and heated at 80 °C for the time indicated in Table 1. The crude mixture was diluted with  $CH_2Cl_2$  (2 mL) and filtered. The insoluble catalytic material **M1** was washed several times with  $CH_2Cl_2$  (3×3 mL), and the combined filtrates were concentrated under vacuum to yield the desired product **6**. The recovered catalytic material **M1** (which had a pinkish color) was dried under vacuum and used directly in the next cycle (a new loading of AgBF<sub>4</sub> was needed). Spectral data of compound-s **6a–e** were in accordance with those described in the literature.<sup>[10]</sup>

# Procedure for the cycloisomerization of 4-pentynoic acid (7 a) catalyzed by 2

To a biphasic system composed of toluene (1 mL) and distilled water (1 mL), **7a** (0.3 mmol) and catalyst **2** (2.5 mol% Au) were added. The mixture was stirred magnetically under air at RT until the complete conversion of the alkynoic acid was observed by TLC (hexane/AcOEt 9:1). The organic phase was then separated, the aqueous layer was extracted with Et<sub>2</sub>O (3×1.5 mL), and the combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and filtered through a short pad of silica gel using dichloromethane as the eluent. The volatiles were removed under vacuum to yield **8a**.

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# General procedure for the cycloisomerization of $\gamma$ -alkynoic acids catalyzed by M1 in toluene/water

To a biphasic system composed of toluene (0.5 mL) and distilled water (0.5 mL), the alkynoic acid (0.15 mmol) and catalyst **M1** (2.5 mol% Au) were added. The mixture was stirred by using a laboratory wrist-type shaker apparatus under air at RT until the complete conversion of the alkynoic acid was observed by using TLC (hexane/AcOEt 9:1). The organic phase was then separated, the aqueous layer was extracted with Et<sub>2</sub>O ( $3 \times 1.5$  mL), and the combined organic extracts were dried over anhydrous MgSO<sub>4</sub>. The volatiles were removed under vacuum to yield the corresponding lactone **8**. Recyclability tests were performed by recharging the system (water+white solid **M1**) with toluene and the corresponding alkynoic acid. The identity of lactones **8a**-**c** and **8d/8d'** was assessed by comparison of their <sup>1</sup>H and <sup>13</sup>C NMR spectra with those reported in the literature.<sup>[8a,26]</sup>

# General procedure for the cycloisomerization of $\gamma$ -alkynoic acids catalyzed by M1 in DES

Alkynoic acid **7** (0.15 mmol) was dissolved in 1 ChCl/2 Urea (0.150 g) in a vial and then heterogeneous catalyst **M1** (2.5 mol% Au) was added. The mixture was stirred magnetically under air at RT until the complete conversion of the alkynoic acid was observed by using TLC (hexane/AcOEt 9:1). The reaction mixture was then extracted with Et<sub>2</sub>O (3×1.5 mL), and the combined organic extracts were dried over anhydrous MgSO<sub>4</sub>. The volatiles were removed under vacuum to yield the corresponding lactone **8**. Recyclability tests were performed by recharging the system (DES+solid **M1**) with the corresponding alkynoic acid.

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## **FULL PAPERS**



**Golden gels:** The first silica-supported (NHC)AuCl (NHC = N-heterocyclic carbene) complex prepared by a sol-gel process from a well-defined bis-silylated precursor is an active and recyclable catalyst for rearrangement and cycloisomerization reactions. M. Ferré, X. Cattoën, M. Wong Chi Man, R. Pleixats\*



Sol–Gel Immobilized N-Heterocyclic Carbene Gold Complex as a Recyclable Catalyst for the Rearrangement of Allylic Esters and the Cycloisomerization of γ-Alkynoic Acids