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Stabilization and recovery of gold catalysts in the cyclopropanation of alkenes within ionic liquids

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ABSTRACT

Au(I) and Au(III) salts ($NaAuCl_4$ and $KAuCN_2$ respectively) were found to be active catalysts for the cyclopropanation of alkenes with ethyldiazoacetate, in many cases affording high yields of cyclopropanecarboxylates. But these gold salts rapidly decomposed and agglomerated when working with organic solvents, resulting in less active and less selective gold metal particles. With ionic liquids (ILs) as solvents, the gold catalysts were stabilized, especially Au(I), and products and catalyst separation and recycling could be achieved. In both cases, $NaAuCl_4$ and $KAuCN_2$ underwent reductive transformation to Au(0) to afford gold nanoparticles, which remained stabilized in the IL, behaving as an authentic metal nanoparticle reservoir. It was found that cyclopropanation and aromatic addition were sensitive to gold particle size, whereas the formation of fumarate and maleate esters was insensitive to gold particle size.

1. Introduction

Gold has been shown to be an active and selective catalyst for numerous reactions, including C–C [1–5], C–N [6–10], C–O [11,12], C–H [13–15], and C–Si [16] bond-forming reactions; oxidation [17]; and enantioselective hydrogenation of olefins and imines [18,19]. In many cases, gold salts have good activity and selectivity, but have drawbacks associated with catalyst recovery and recycling and, even more importantly, in many cases can decompose during the reaction, leading to the formation of large particles of gold metal that are not active or unselective. Thus, it is of interest to find a procedure to stabilize the gold salts and avoid decomposition while achieving easy separation of the reaction products and catalyst recycling.

The transition metal-catalyzed transfer of carbene units from diazo compounds to alkenes provides a powerful organic synthesis tool for obtaining cyclopropane derivatives, which are important intermediates for the construction of relatively complex molecules [20–27]. Cyclopropanation of alkenes from diazo compounds can be catalyzed by Cu(I) [23]. Because the external electronic structure of Cu(I) is similar to that of Au(I), gold possibly could be a suitable cyclopropanation catalyst. Indeed, the literature reports that a gold(I)-based catalyst also can be an efficient and chemoselective catalyst for this reaction [28]. Here we demonstrate that Au(I) as well as Au(III) salts ($KAuCN_2$ and $NaAuCl_4$) can catalyze the cyclopropanation of alkenes by ethyldiazoacetate in ionic liquids (ILs) as reaction media. We show that when the same gold salt catalysts are used in the presence of the appropriated IL, the Au(III) and Au(I) salts can be stabilized toward the formation of gold metal agglomerates, thereby resulting in higher yields of cyclopropanes than can be achieved using conventional solvents. Moreover, the separation of products and catalyst recovery and recycling is much easier when using ILs.

2. Experimental

2.1. Materials and starting reagents

The starting reagents (alkenes and ethyldiazoacetate) and catalysts $NaAuCl_4 \cdot 2H_2O$ and $KAuCN_2$ were purchased from Aldrich. [MOIM] PF_6, with purity of 99.9% and water content of 182.3 ppm, was supplied by Fluka. Halides and sulfates ions were not detected. [BMIM] PF_6, with purity $>98.5\%$, water content $<0.02\%$, and halogen content (as chloride) <10 mg/kg, was supplied by Solvent Innovation. [BMIM] BF_4, with purity $>98.5\%$, water content $<0.02\%$, and anion traces (bromide $\leqslant 25$ mg/kg; chloride $\leqslant 25$ mg/kg; nitrate $\leqslant 25$ mg/kg and phosphate $\leqslant 10$ mg/kg), was supplied by Solvent Innovation. [BMIM] Br, with purity $>97.0\%$ and water content $<1\%$, was supplied by Solvent Innovation.

2.2. General techniques

Room temperature UV–vis spectrum of a chloroform solution of catalyst containing IL [BMIM] PF_6 was recorded with a Shimadzu UV–vis scanning spectrophotometer. The size distribution profile of small gold nanoparticles was determined using a Nano Zetasizer Malvern (ZEN3600) MPT-2 analyzer (with a red laser wave-

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length of 633 nm). At least two measurements were obtained for each sample, and the final Z-average is given as an average value (see Supplementary material). Raman spectra were obtained with an "in via" Renishaw spectrometer, equipped with a microscope (Olympus). The exciting wavelength was 785 nm from a Renishaw HPNIR laser with a power of ca. 15 mW on the sample. Solution NMR spectra were recorded with a Bruker Avance 300 spectrometer at 300.13 MHz (^{1}H), 75.47 MHz (^{13}C), and 121.49 MHz (^{13}P). ^{1}H and ^{13}C NMR spectra of isolated cyclopropanecarboxylates were recorded in Cl_3CD. ^{13}P NMR spectra of gold-containing ILs were obtained in DMSO-d_6. The gold content of ILs was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian 715-ES spectrometer.

2.3. Synthesis of thiol-stabilized gold nanoparticles (1–3 nm)

The thiol-derived gold nanoparticles were prepared as described previously [29]. The resulting material was handled as a simple chemical compound.

2.4. General procedure for the cyclopropanation reactions

To a stirred solution of alkene (3 mmol), 8% mol of the $NaAuCl_4$ catalyst (or 5% mol $KAuCN_2$ or 8% mol $CuCl_2$) and the IL (3 ml), ethyldiazoacetate (1 mmol), was added either completely before starting the reaction or slowly in a dropwise manner over 2 h. The resulting mixture was stirred at room temperature for 24 h. After the reaction was completed, the reaction mixture was extracted with diethyl ether (1 × 10 ml). The organic solvent was dried with anhydrous $MgSO_4$ and concentrated under vacuum. The samples were analyzed by gas chromatography.

Cyclopropanecarboxylates were isolated by column gas chromatography on silica gel (Merck, 100–200 mesh; ethyl acetate–hexane 1:9). They were purified and identified by comparison of their NMR-^{1}H, NMR-^{13}C and mass spectra with literature values. The spectral data of all products were identical to those of authentic samples.

3. Results and discussion

Gold(III)-catalyzed carbene transfer reaction from ethyldiazoacetate (EDA) to styrene was initially carried out in the presence of $NaAuCl_4$ but in the absence of solvent. Under these experimental conditions, the *cis/trans*-cyclopropanecarboxylates were obtained with low selectivity (see entry 1 in Table 1) due to the formation of relatively large amounts of EDA dimerization products (diethyl fumarate and maleate), together with *o*-, *m*-, *p*-aromatic addition products (Scheme 1).

The formation of these three isomers can be accounted for by a formal insertion of the $:CH_2COOEt$ carbene into the sp^2 C–H aromatic bond [28].

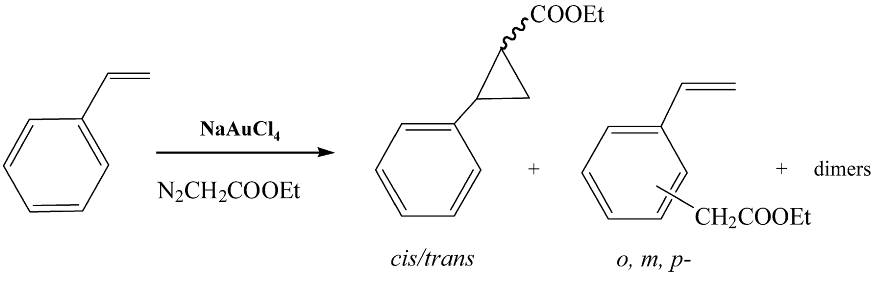
The influence of solvent on activity and chemoselectivity of cyclopropanation was studied using solvents with different polarities. The findings, given in Table 1, show that independent of the solvent, high conversions could be achieved in all cases, whereas chemoselectivity to *cis/trans*-cyclopropanecarboxylates clearly was much higher for the less-polar toluene (entries 2–6, Table 1). Regardless of the solvent used, $NaAuCl_4$ decomposed slowly during the addition of EDA, and metallic gold formed as a thin golden "mirror" that could be recovered at the end of reaction.

Because the gold particles formed by catalyst decomposition may very well also be catalytically active but less selective toward the formation of cyclopropanes, we carried out a control experiment in which styrene and EDA were allowed to react in the presence of metal gold nanoparticles (1–3 nm) freshly prepared as described previously [29]. Despite the fact that gold nanoparticles stabilized by surface halide ions are likely to be the best model for studying the activity of metal nanoparticles, we prepared colloidal gold nanoparticles capped with thiols, given that gold nanoparticles are usually surrounded with monolayers of organic molecules when prepared in organic solvents, whereas nanoparticles sta-

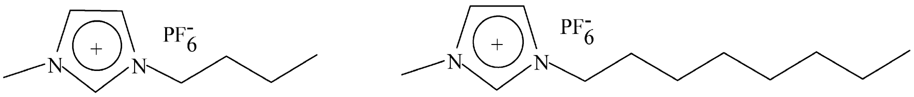
Table 1
Cyclopropanation reaction of styrene catalyzed by $NaAuCl_4$ with ethyldiazoacetate (EDA) in different solvents at room temperature

Entry	Solvent	Conv. (%)[a]	Yield (%)			TON[e]
			cis/trans[b]	*o*-, *m*-, *p*-[c]	Dimers[d]	
1	–	97	21/28	30	20	17.3
2	CH_3CN	93	16/29	12	–	11.9
3	CH_3NO_2	91	16/32	16	1	7.9
4	1,2-Dichloroethane	85	22/29	21	2	10.5
5	CH_2Cl_2	96	25/39	25	10	12.5
6	Toluene	91	32/40	26	2	14.5
7	Toluene[f]	87	3/28	18	–[g]	16

[a] Based in EDA consumption and determined by GC after total consumption of EDA with *n*-dodecane as internal standard.
[b] Cyclopropanecarboxylate isomers (*cis* + *trans*).
[c] Addition aromatic products at the *ortho*-, *meta*- and *para*-position (*o*-, *m*-, *p*-).
[d] Diethyl fumarate and maleate.
[e] Calculated as mmol of converted substrate/mmol of catalyst.
[f] *n*-Dodecanethiol stabilized Au(0) nanoparticles (1–3 nm) as catalyst in toluene as solvent reaction [29].
[g] Unidentified products of high molecular weight were detected by GC (instead of fumarate and maleate esters).



Scheme 1. Carbene transfer reaction from EDA to styrene catalyzed by $NaAuCl_4$.



[BMIM] PF_6 **[OMIM] PF_6**

Fig. 1. Structure of ionic liquids used in this study.

Table 2
Cyclopropanation reaction of alkenes with ethyldiazoacetate (EDA) catalyzed by $NaAuCl_4$ in ionic liquids at room temperature

Entry	Alkene	Solvent	Conv. (%)[a]	Yield (%)			TON[e]
				cis/trans[b]	*o*-, *m*-, *p*-[c]	Dimers[d]	
1	Styrene[f]	[BMIM] PF_6	98 (99)	32/62 (30/63)	2 (1)	2	10 (13)
2	Styrene[g]	[BMIM] PF_6	85	20/29	12	2 (24)[h]	11.4
3	Styrene[i]	[BMIM] PF_6	29	2/0	9	–	6
4	Styrene[j]	[BMIM] PF_6	91	32/49	7	–	11
5	Styrene[k]	[BMIM] PF_6	99	29/52	11	7	23.5
6	Styrene[l]	[BMIM] PF_6	99	34/38	6	21	21
7	*p*-Methoxystyrene	[BMIM] PF_6	90	8/19	3	4	7.2
8	*p*-Trifluoromethylstyrene[f]	[BMIM] PF_6	99 (94)	2/3 (37/40)	1 (4)	–	9 (12)
9	β-Methylstyrene	[BMIM] PF_6	82	67[m]	–	–	10
10	α-Methylstyrene[f]	[BMIM] PF_6	100 (98)	– (41/43)	– (4)	–	– (13)
11	Cyclooctene	[BMIM] PF_6	78	27[m]	6	5	12.3
12	Styrene[f]	[OMIM] PF_6	86 (99)	1/83 (35/59)	2 (2)	– (2)	7.4 (11)
13	*p*-Trifluoromethylstyrene[f]	[OMIM] PF_6	83 (95)	32/40 (40/42)	– (3)	– (3)	7.4 (13)
14	β-Methylstyrene	[OMIM] PF_6	83	79[m]	4	–	5
15	*p*-Methoxystyrene	[OMIM] PF_6	75	10/22	3	–	5
16	α-Methylstyrene[f]	[OMIM] PF_6	59 (99)	15/19 (44/44)	1 (4)	– (3)	8.3 (12)

[a] Based in EDA consumption and determined by GC after total consumption of EDA with *n*-dodecane as internal standard.
[b] Cyclopropanecarboxylates (*cis* + *trans*).
[c] Addition aromatic products at the *ortho*-, *meta*- and *para*-position (*o*-, *m*-, *p*-).
[d] Diethyl fumarate and maleate.
[e] Calculated as mmol of converted substrate/mmol of catalyst.
[f] Results in parenthesis refer to experiments in which EDA was completely added before starting the reaction.
[g] Reaction carried out at 60 °C.
[h] Oligomerization products in parenthesis.
[i] HCl as catalyst.
[j] Ionic liquid treated at 70 °C under reduced pressure for 8 h.
[k] $NaAuCl_4 \cdot 2H_2O + CuCl_2$.
[l] $CuCl_2$.
[m] Σ stereoisomers.

bilized with halides are usually prepared in aqueous medium. Thus, a catalytic amount of gold nanoparticles (stabilized with *n*-dodecanethiol) was added to fresh toluene and styrene. EDA was slowly added, and the reaction was monitored by GC.

The results obtained with gold nanoparticles after 24 h demonstrate lower conversion and yield of cyclopropanecarboxylates than those achieved using $NaAuCl_4$ as catalyst in the same solvent, toluene (entry 7, Table 1). This suggests that the low selectivity toward cyclopropanes obtained in organic solvents may not be due solely to the Au(III) catalyst, but also may be related to the formation of metallic gold by decomposition of the catalyst that directs the reaction toward the unwanted products. If this indeed is the case, then it would be necessary to increase the stability of the salt during the reaction to increase the selectivity of the process. We return to this point later in the paper.

3.1. Cyclopropanation reactions catalyzed by $NaAuCl_4$ and $KAuCN_2$ in ILs as solvents

ILs are being used as potential green replacements for conventional organic solvents due to their negligible vapor pressure and the possibility of tuning their physicochemical properties through structural modification of the cation and choice of anion [30–39]. More recently, the IL 1-butyl-3-methylimidazolium hexafluorophosphate (commonly abbreviated as [BMIM] PF_6) has shown the ability to stabilize palladium nanoparticles without the need to add stabilizing agents to avoid the typical metal agglomeration [40]. If this is so, then it also may be possible to stabilize Au(III) species in an IL better than can be done with organic solvents. To begin, we chose [BMIM] PF_6 and the even more hydrophobic 1-methyl-3-octylimidazolium hexafluorophosphate [MOIM] PF_6 to carry out the cyclopropanation reaction (see Fig. 1).[1]

Results from Table 2 (entry 1) show that with [BMIM] PF_6, it is possible to obtain better selectivities and yields to cyclopropanation products than with any of the organic solvents used before. Moreover, the yields of cyclopropanecarboxylates obtained from aromatic alkenes, such as styrene, are much higher than those reported in the literature for a known gold(I) catalyst [28]. The evolution of the products during reaction was followed by taking samples at different time intervals (Fig. 2). The IL [BMIM] PF_6 was extracted with diethyl ether.[2]

Fig. 2 shows that the yield of *cis* + *trans*-cyclopropanes increased rapidly up to ~80% during the first 8 h, then continued to increase up to 94% over 24 h. In contrast, the yield of aromatic addition products remained constant up to the completion of the reaction.

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[1] PF_6^- provides hydrophobicity to the imidazolium based IL with respect to other counter anions, such as BF_4^-, Cl^-, etc. Similarly the use of long tail substituents at the cation may contribute to increase even further this property.

[2] [BMIM] PF_6 is fully miscible with polar organic solvents such as ethanol, dimethylsulfoxide, acetonitrile, acetone, etc., being at the same time fully or partially immiscible in less polar organic solvents such as toluene, hexane, diethyl ether, etc.

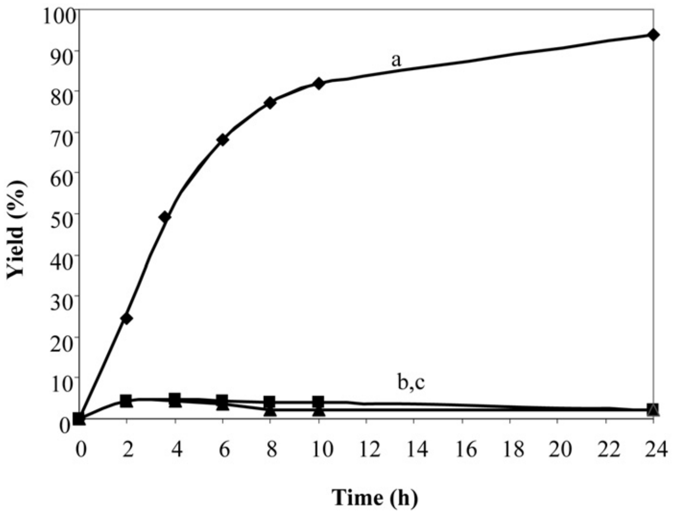

Fig. 2. Evolution of different products with time in the cyclopropanation reaction of styrene with EDA catalyzed by $NaAuCl_4$ in the ionic liquid [BMIM] PF_6: (a) *cis* + *trans*-cyclopropanes; (b) addition aromatic products (*o*-, *m*-, *p*-) and (c) dimers (entry 1, Table 2).

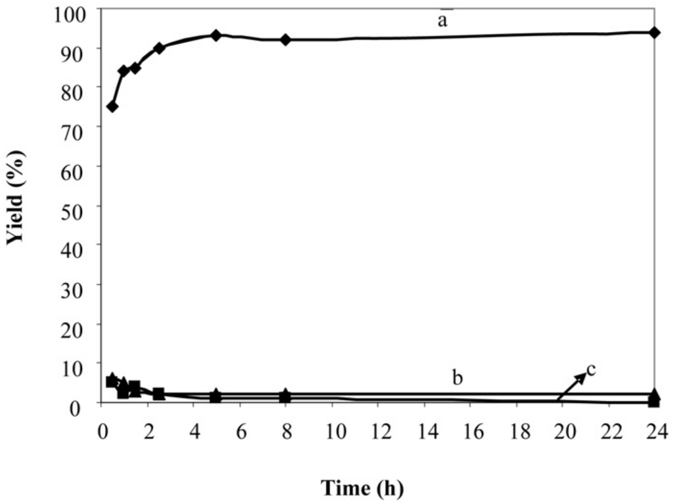

Fig. 3. Plot showing the yields of reaction products *versus* time in the cyclopropanation reaction of styrene with EDA (immediate complete addition) catalyzed by $NaAuCl_4$ in the ionic liquid [BMIM] PF_6: (a) *cis* + *trans*-cyclopropanes; (b) addition aromatic products (*o*-, *m*-, *p*-) and (c) others.

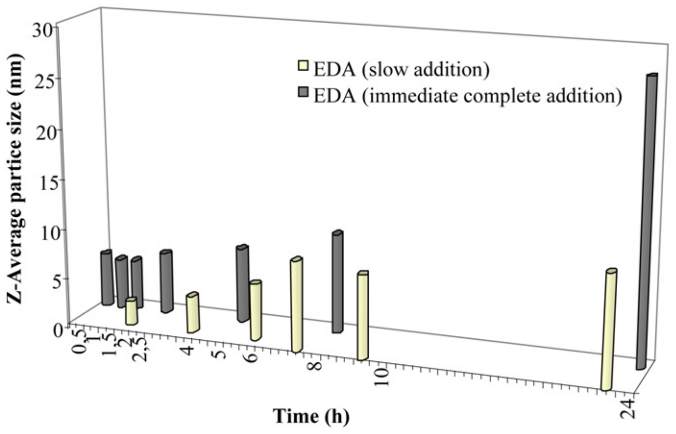

Fig. 4. Particle size for gold nanoparticles measured as a function of time in the cyclopropanation reaction of styrene catalyzed by $NaAuCl_4$ upon (a) slow addition of EDA and (b) immediate complete addition of EDA in [BMIM] PF_6 as solvent.

A control reaction between styrene and EDA was performed in the absence of catalyst in the IL [BMIM] PF_6 at 20 °C and no cyclopropanation was observed.

The addition time of EDA (i.e., concentration of EDA in the reaction mixture) should be considered as a possibly important variable in cyclopropanation reactions, because the metal carbene intermediate can interact with another diazoester molecule (rather than with the olefin) to form a dimer. This is the reason why decreasing the rate of EDA addition should, in principle, result in better cyclopropane yields and explains why numerous studies in the literature use long addition times at the start of the reaction [23]. If this were the case, then the selectivity toward cyclopropanes would be expected to increase with an increasing styrene:EDA ratio, because the greater this ratio, the more likely that the metal carbene intermediate will interact with styrene rather than with another carbene to form a dimer. In most cases (as in our case), both parameters can be adjusted simultaneously; indeed, we used a long duration of EDA addition (2 h) and an excess of olefin to carry out the reactions (see Section 2). We also studied the effect of adding all of the EDA at the beginning of the reaction on the cyclopropanation reaction of styrene catalyzed by $NaAuCl_4$ in [BMIM] PF_6, with the idea that the high viscosity of ILs might slow dimer formation (see Fig. 3). In this experiment, the reaction was almost completed within 6 h, and, more interestingly, the yields of the EDA coupling products (fumarate and maleate) were undetectable (Fig. 3). Another interesting finding was that nearly identical yields of *cis* + *trans*-cyclopropanes were obtained with respect to the experiment in which EDA was added slowly during the first 2 h of the reaction period. This finding is very important, because the reaction time for cyclopropanation was shortened considerably and also the catalyst working time was extended considerably, because the catalyst could be reused more times before unactive metal agglomerates formed.

Closely connected to that experiment, we also compared the possible effect of either an initial complete addition or slow addition of EDA on the kinetics of gold nanoparticle formation in [BMIM] PF_6 as solvent. We used dynamic light scattering (DLS)[3] [41] to evaluate the size of gold particles that could form with $NaAuCl_4$ in the IL [BMIM] PF_6 (see Section 2 and Fig. 4). Fig. 4 shows that the slow addition of diazocompound not only suppressed the dimerization reaction of EDA (although this may not be necessarily the case with [BMIM] PF_6 as solvent), but also contributed to slowing the growth of gold nanoparticles during the reaction.

Taking into account a previous study in which the reaction between alcohols and alkenes was catalyzed by $AuCl_3$ and the rate of decomposition and metal formation was slowed by introduction of $CuCl_2$ [11], we performed the cyclopropanation reaction in the presence of $NaAuCl_4$ and $CuCl_2$ as co-catalysts in the IL [BMIM] PF_6 as solvent (entry 5, Table 2). Contrary to our expectations, the selectivity to cyclopropanation was lower here than in the absence of $CuCl_2$. Nevertheless, when we carried out the reaction in the presence of $CuCl_2$ (without $NaAuCl_4$), $CuCl_2$ clearly was also active but less selective than Au(III) for performing the cyclopropanation reaction in the IL, accounting for the loss of selectivity observed (entry 6, Table 2).

To evaluate the scope of this gold-catalyzed reaction, we studied the reactivity of other electron-rich and electron-deficient

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[3] Fundamentals of this technique (also known as Photon Correlation Spectroscopy) are based on the fact that particles, emulsions and molecules in suspension undergo Brownian motion. If the particles or molecules are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes–Einstein relationship.

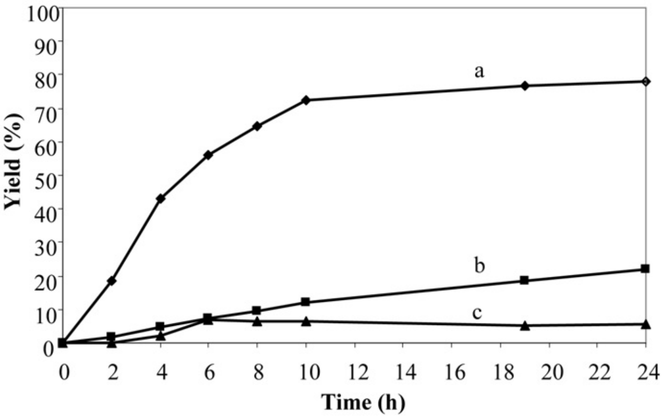


Fig. 5. Evolution of different products with time in the cyclopropanation reaction of styrene with EDA catalyzed by $KAuCN_2$ in the ionic liquid BMIM PF_6: (a) *cis* + *trans*-cyclopropanes; (b) addition aromatic products (*o*-, *m*-, *p*-), (c) others.

styrene derivatives (*p*-methoxystyrene and *p*-trifluoromethylstyrene, respectively). In this case, both olefins converted almost completely, although giving very low yields of cyclopropanecarboxylates. Although the substituents at this *para*-position (methoxy and trifluoromethyl) hindered the insertion of the CH_2COOEt unit into the aromatic ring, this did not contribute to an increased yield of the desired cyclopropanecarboxylates (see entries 7 and 8, Table 2).

With β-methylstyrene, good conversion values could be achieved after 24 h of reaction, and neither addition aromatic products nor fumarate and maleate esters were detected by GC (entry 9, Table 2). α-Methylstyrene converted almost completely, giving a complex mixture of unidentified products (entry 10, Table 2). Finally, we also screened the carbene transfer reaction from EDA into the aliphatic olefin *cis*-cyclooctene (entry 11, Table 2), and found that in this case, low yields of the corresponding cyclopropanecarboxylates could be achieved.

We also studied the effect of an initial complete addition of EDA on the cyclopropanation reaction of alkenes α-methylstyrene and *p*-trifluromethylstyrene catalyzed by $NaAuCl_4$ in [BMIM] PF_6 (see entries 8 and 10 in Table 2). The reaction was much faster (completed in 1 h in both cases), and the cyclopropane yields were improved significantly with respect to the experiments in which EDA was added slowly over 2 h (see Table 2). Even more importantly, no dimer formation was detected.

The cyclopropanation reaction of styrene derivatives when catalyzed by $NaAuCl_4$ in the IL [MOIM] PF_6 resulted in much better yields of cyclopropanecarboxylates than those achieved when these reactions were carried out in [BMIM] PF_6 (see entries 12–16, Table 2). The most significant feature with [MOIM] PF_6 was the almost exclusive formation of the *trans*-cyclopropanecarboxylate in the case of styrene (entry 12, Table 2).

Again, we evaluated the possible influence of an immediate complete addition of EDA in [MOIM] PF_6 IL. To do so, we used the cyclopropanation of α-methylstyrene and *p*-trifluoromethylstyrene with $NaAuCl_4$. As in the study with [BMIM] PF_6, the reaction was completed rather rapidly, affording high yields of cyclopropanecarboxylates in both cases (4 and 2 h for α-methylstyrene and *p*-trifluoromethylstyrene, respectively). Minor amounts of fumarate an maleate dimers were detected by GC analysis in both cases (see entries 13 and 16 in Table 2). Similarly, with $KAuCN_2$ as catalyst and [BMIM] PF_6 as solvent, the yields of cyclopropanecarboxylates derived from styrene were again higher than those reported in the literature for a related gold(I) complex (entry 1, Table 3) [28].

Fig. 5 shows the evolution of different reaction products over time for the cyclopropanation reaction of styrene with EDA catalyzed by $KAuCN_2$ in [BMIM] PF_6. The figure indicates that the yield of *cis* + *trans*-cyclopropanes increased to approximately 70% during the first 10 h, then it increased slightly to 78% after 24 h. Similarly, the yield of aromatic addition products increased smoothly, reaching a maximum after 24 h.

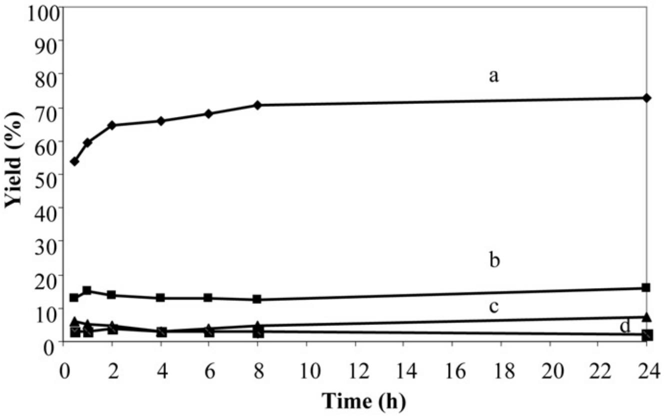


Fig. 6. Plot showing the yields of reaction products *versus* time in the cyclopropanation reaction of styrene with EDA (immediate addition) catalyzed by $KAuCN_2$ in the ionic liquid BMIM PF_6: (a) *cis* + *trans*-cyclopropanes; (b) addition aromatic products (*o*-, *m*-, *p*-), (c) others and (d) dimers (fumarate and maleate esters).

We also studied the effect of adding the total amount of EDA when starting the reaction on the cyclopropanation reaction of styrene in [BMIM] PF_6 with $KAuCN_2$ as the catalyst (Fig. 6). The results show that the reaction was almost completed in 8 h, demonstrating that the yields of the EDA-coupling products (fumarate and maleate) also were very low (Fig. 6). As in the case of $NaAuCl_4$, nearly identical yields of *cis* + *trans*-cyclopropanes were obtained with respect to the experiment in which EDA was added in 2 h at the start of the reaction period (cf. Fig. 5).

We have seen that when water (10% mol) was added in the cyclopropanation of styrene with $KAuCN_2$ as catalyst, the yield of cyclopropanes decreased slightly with respect to the experiment in the absence of water (see entries 1 and 2 in Table 3), indicating that possible differences in the water present within the reaction media accompanying the catalysts, reactants, or ILs should have a small influence on reactivity.

Similarly, the cyclopropane yields were significantly higher for the alkenes α-methylstyrene, *p*-trifluoromethylstyrene, and cyclooctene compared with those obtained with $NaAuCl_4$ as catalyst in the same IL (entries 2, 3, and 5, Table 3). In striking contrast, *p*-methoxystyrene afforded poorer results in cyclopropanation (see entry 4, Table 3).

With the exception of β-methylstyrene, the results obtained in cyclopropanation reactions with $KAuCN_2$ as catalyst improved when the catalyzed reactions were carried out in [MOIM] PF_6 as solvent (see entries 6–10, Table 3). In this case, the most remarkable features with $KAuCN_2$ were the absence of typical EDA dimerization products (especially when the diazocompound was added slowly) and the higher yields of aromatic addition products with respect to the Au(III) catalyst $NaAuCl_4$ (cf. Tables 2 and 3).

We studied the effect of adding all of the EDA when starting the reaction for reactions catalyzed by $KAuCN_2$ in both ILs [BMIM] PF_6 and [MOIM] PF_6 with α-methylstyrene and *p*-trifluoromethylstyrene as model olefins. As in previous cases, the reactions were completed in a few hours (6–12 h) and afforded high yields of cyclopropanecarboxylates in all cases (see entries 3, 4, 8 and 10 in Table 3).

3.2. Stability of ILs in the presence of $NaAuCl_4$ and $KAuCN_2$

As stated earlier, the catalyst evaluation revealed enhanced activity and chemoselectivity of $[AuCl_4]^-$ for the cyclopropanation

Table 3
Cyclopropanation reaction of alkenes catalyzed by $K(CN)_2Au$ with ethyl diazoacetate (EDA) in ionic liquids at room temperature

Entry	Alkene	ILs	Conv. (%)[a]	Yield (%)		TON[d]
				cis/trans[b]	*o*-, *m*-, *p*-[c]	
1	Styrene[e]	[BMIM] PF_6	100 (98)	32/46 (30/43)	22 (16)	8 (11)
2	Styrene[f]	[BMIM] PF_6	95	29/32	15	8
3	α-Methylstyrene[e]	[BMIM] PF_6	97 (96)	15/53 (40/43)	28 (7)	7 (14)
4	*p*-Trifluoromethylstyrene[e]	[BMIM] PF_6	99 (93)	3/27 (31/39)	17 (2)	16 (13)
5	*p*-Methoxystyrene	[BMIM] PF_6	98	1/2	–	10
6	Cyclooctene	[BMIM] PF_6	100	68[g]	28	6.3
7	Styrene[e]	[OMIM] PF_6	98	34/44	22	5.8(12)
8	α-Methylstyrene[e,h]	[OMIM] PF_6	100 (96)	51/18 (40/47)	17 (5)	7.7 (13)
9	*p*-Methoxystyrene	[OMIM] PF_6	100	15/68	15	8.9
10	*p*-Trifluoromethylstyrene[e,f]	[OMIM] PF_6	100 (93)	10/12 (36/40)	27 (4)	7.7 (15)
11	β-Methylstyrene	[OMIM] PF_6	100	55[e]	4	9.1

[a] Based in EDA consumption and determined by GC after total consumption of EDA with *n*-dodecane as internal standard.
[b] Cyclopropanecarboxylate diastereomers (*cis* + *trans*).
[c] Addition aromatic products at the *ortho*-, *meta*- and *para*-position (*o*-, *m*-, *p*-).
[d] mmol converted substrate/mmol catalyst.
[e] Results in parenthesis refer to experiments in which EDA was completely added before starting the reaction.
[f] 10% mol water was added.
[g] Σ stereoisomers.
[h] Minor amounts of dimers were detected (<2%).

reaction in the IL [BMIM] PF_6 compared with other conventional solvents. Nevertheless, we note that [BMIM] PF_6 became acidic shortly after $AuCl_4^-$ was added, suggesting that either the Au(III) salt or PF_6^- anions may hydrolyze under these experimental conditions [42–44]. Hydrolysis of $AuCl_4^-$ can effectively account for the existence of $AuCl_4^-$ in pH- and strength-dependent equilibrium with gold species (vs $AuCl_3OH^-$ and $AuCl_3(H_2O)$, among others) with simultaneous HCl formation [42].

Similarly, PF_6^- anions can undergo hydrolysis to give phosphates and HF [43,44]. The formation of these compounds then may contribute to acid-catalyzed reactions or initiate catalyst degradation. In connection with this, we carried out a control reaction in the presence of HCl (but in the absence of tetrachloroaurate) to evaluate the influence of mineral acids in the cyclopropanation reaction. We found that the olefin (styrene) converted rather sluggishly (up to 29%) after 24 h of reaction and that the yield of cyclopropane products was very low (2%) (entry 3, Table 2). In this case, a complex mixture of unidentified products of high molecular weight was detected by gas chromatography (entry 3, Table 2).

The acidity of the reaction medium sometimes may cause side reactions. In the case of cyclopropanation of styrene derivatives, the selectivity toward cyclopropanes depends in part on the acidity of the reaction medium, given that acid catalysts are able to promote the cationic polymerization of styrene derivatives. Examples of this effect are described in the literature. For instance, in cyclopropanation reactions catalyzed by solid copper catalysts, the lowest selectivities toward cyclopropanes were achieved when acidic K-montmorillonite was used as the support [45].

We used ^{31}P NMR spectroscopy to detect the formation of products derived from a plausible PF_6^- hydrolytic reaction that could generate acid molecules. In this experiment, an equimolar mixture of [BMIM] PF_6 and $NaAuCl_4$ was submitted to vigorous stirring at room temperature under nitrogen for 2 h, after which the ^{31}P NMR spectrum of this mixture was recorded. Through analysis of this ^{31}P spectrum (Fig. 7A), three different species derived from the hydrolysis of PF_6^- could be detected: a triplet with chemical shift at $\delta^{31}P = -15.77$ ppm [$J(P,F) = 953.4$ Hz], a doublet with $\delta^{31}P = -6.89$ ppm [$J(P-F) = 911.82$ Hz], and a singlet at 0 ppm. The first two signals were tentatively assigned to $PO_2F_2^-$ and PO_3F^{2-}, respectively [46], whereas the singlet was assigned to H_3PO_4 (an acid that could be formed in the final stage of the hydrolysis). The septet with $\delta^{31}P = -143.8$ ppm [$J(P-F) = 711.33$ Hz] belongs to PF_6^- [46].

In parallel, and to avoid the undesired PF_6^- hydrolysis, we tried to exclude moisture from [BMIM] PF_6 by heating the IL at 70 °C under reduced pressure (10^{-3} mbar) for 8 h [47]. Results for the cyclopropanation of styrene with EDA with $NaAuCl_4 \cdot 2H_2O$ as the catalyst are given in Table 2 (see entry 4). As can be deduced from these results, the yields of cyclopropanecarboxylates in [BMIM] PF_6 after 24 h did not improve significantly after drying compared with the results obtained without the exclusion of water. Nonetheless, the most remarkable feature in this case is that GC did not detect the formation of fumarate and maleate esters (see entries 1 and 4 in Table 2). Contrary to our expectations, the more hydrophobic nature of [MOIM] PF_6 did not completely prevent PF_6^- hydrolysis in the presence of some water. The same species, $PO_2F_2^-$, PO_3F^{2-}, and H_3PO_4 were detected by ^{31}P NMR when the spectrum of a mixture of $NaAuCl_4$ and [MOIM] PF_6 was recorded under identical experimental conditions (see Fig. 7B).

We note that a possible reaction between imidazolium cations (in the IL) and $AuCl_4^-$ may occur simultaneously to form a gold N-heterocyclic carbene complex, as has been described previously for palladium [48]. But we discounted this possibility, because formation of a similar gold carbene complex was not detected by ^1H NMR, despite the fact that equimolar amounts of tetrachloroaurate(III) salt and [BMIM] PF_6 were used to record the ^1H NMR spectrum.

It is worth pointing out to that the counteranion PF_6^- was stable when the gold(I) complex $KAuCN_2$ was added to the ILs [BMIM] PF_6 and [MOIM] PF_6 separately. In fact, the typical hydrolytic species derived from PF_6^- were not detected by ^{31}P NMR spectroscopy in any case. This suggests that Au(III) may be acting as a catalyst in the hydrolysis of PF_6^-, competing with cylopropanation. In this respect, the possibility that gold(III) may catalyze PF_6^- degradation with simultaneous formation of transition metal fluorides cannot be discarded [43].

On the other hand, and to check whether a plausible release of HCN from $KAuCN_2$ may decrease the selectivity in the cyclopropanation reaction, we recorded the ^1H, ^{31}P, and ^{13}C NMR spectra of the IL before and after the cyclopropanation reaction of styrene was completed (see entry 1, Table 3). Again, the ^1H, ^{31}P, and ^{13}C NMR spectra confirmed that the IL did not change after the reaction, suggesting that [BMIM] PF_6 was stable under these reaction conditions.

We conducted an additional experiment in which the cyclopropanation reaction of styrene with EDA was carried out with HCN as the catalyst (generated *in situ* from equimolar amounts

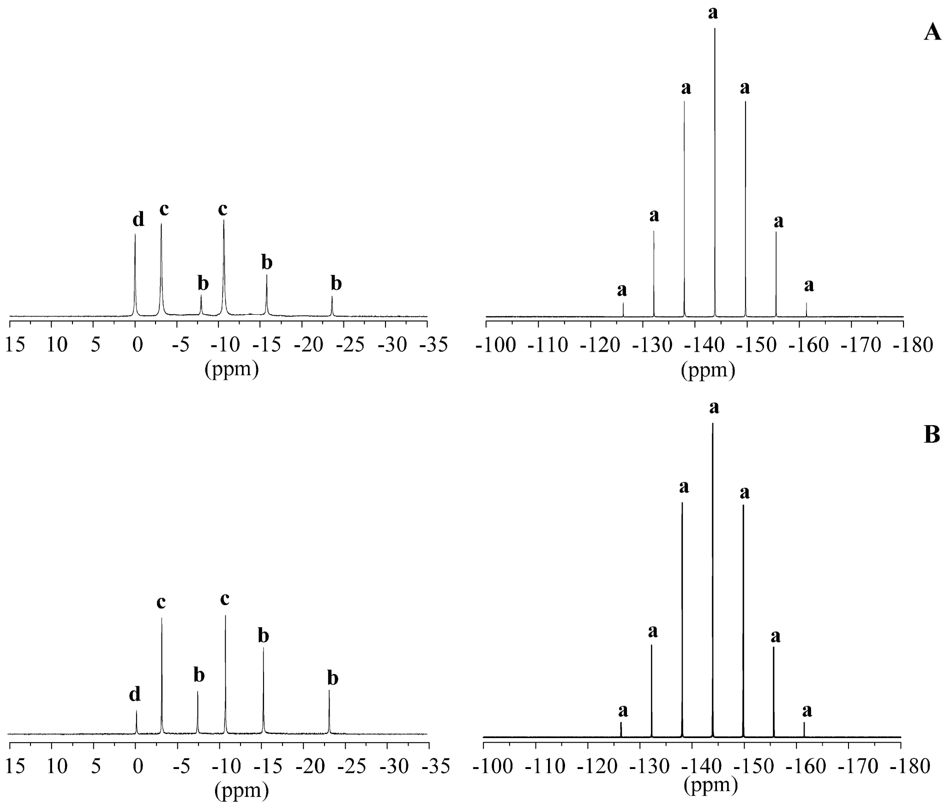


Fig. 7. ^{31}P NMR spectra of two equimolar mixtures of $NaAuCl_4$ and [BMIM] PF_6 (A) and $NaAuCl_4$ and [OMIM] PF_6 respectively (B). Signals a, b, c and d are tentatively assigned to PF_6^-, $PO_2F_2^-$, PO_3F^{2-} and H_3PO_4 respectively.

Table 4
Results obtained in cyclopropanation reaction of styrene with EDA catalyzed by $NaAuCl_4$ in different BMIM based ionic liquids

Entry	Solvent	C (%)[a]	Y (%)				TON[e]
			cis/*trans*[b]	*o*-, *m*-, *p*-[c]	Dimers[d]	Other	
1	BMIM PF_6	98	32/62	2	2	–	10
2	BMIM Br	98	21/7	6	–	64	11
3	BMIM BF_4	86	13/33	4	–	36	11

[a] Based in EDA consumption and determined by GC after total consumption of EDA with *n*-dodecane as internal standard.
[b] Cyclopropanecarboxylates (*cis* + *trans*).
[c] Addition aromatic products at the *ortho*-, *meta*- and *para*-position (*o*-, *m*-, *p*-).
[d] Diethyl fumarate and maleate.
[e] Calculated as mmol of converted substrate/mmol of catalyst.

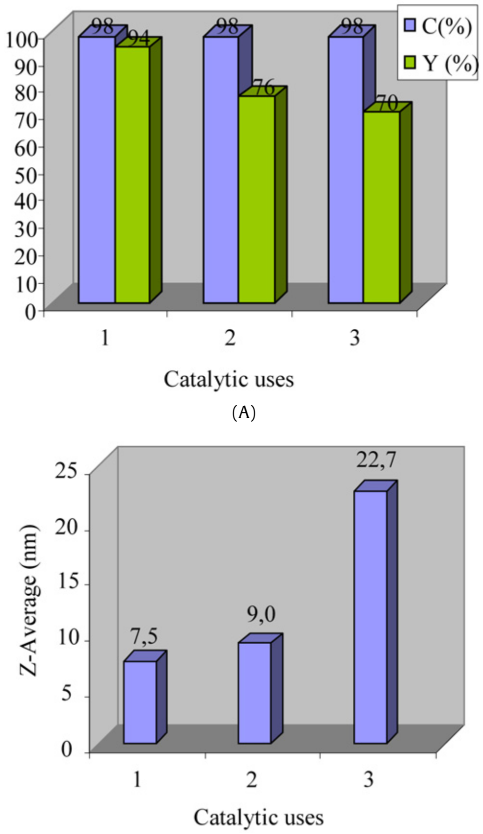
of KCN and water) in [BMIM] PF_6 but in the absence of $KAuCN_2$. In this case, no reaction was observed after 24 h, confirming that HCN did not catalyze the cyclopropanation reaction or any secondary reaction. HCN likely is not sufficiently acidic to promote the cationic polymerization of the olefin styrene under these experimental conditions.

Because the PF_6^- based IL can be partially hydrolyzed in the presence of water, we performed the cyclopropanation reaction in other ILs containing the 1-methyl-3-butyl imidazolium cation but with different anions. Table 4 gives the results obtained for the cyclopropanation reaction of styrene with EDA in [BMIM] Br and [BMIM] BF_4 ILs at room temperature, along with results obtained with BMIM PF_6 for comparison. As can be deduced from this table, the best performance was obtained with [BMIM] PF_6. The more hydrophilic bromide and tetrafluoroborate ILs afforded poorer results on cyclopropanation. It is interesting to note that despite the fact that halide anion (Br^-) tends to stabilize the formation of gold particles, avoiding metal agglomeration, this positive effect has not been reflected in the reaction by increased yields of cyclopropanecarboxylates.

3.3. Reusability and recycling of $NaAuCl_4$ and $KAuCN_2$ catalysts in [BMIM] PF_6

Reusability experiments conducted with $NaAuCl_4$ as the catalyst in [BMIM] PF_6 demonstrated a gradual decrease of chemoselectivity. In this case, the [BMIM] PF_6^- containing catalyst was recycled in a series of consecutive experiments. Fig. 8 shows the comparative conversions and yields of *cis*- and *trans*-cyclopropanation products derived from styrene with repeated cycles. The results indicate that although the rate of salt decomposition may have slowed significantly in [BMIM] PF_6, the gold nanoparticles formed under these experimental conditions grew slowly over time, thereby decreasing the chemoselectivity toward the production of cyclopropanecarboxylates. In this respect, attempts to detect gold nanoparticle formation by Raman spectroscopy were unsuccessful, because the Raman band centered at ca. 265 cm^{-1} and assigned to gold nanoparticles [49] (associated with chloride ions bound to gold nanoparticles) overlapped with a Raman band vibration characteristic of the IL at approximately the same wavenumber.

Nonetheless, the absence of the Au(III)–Cl Raman vibration at 355 cm^{-1} (characteristic of the original complex $NaAuCl_4$) after



(A)

(B)

Fig. 8. (A) Comparative conversions (C%) and yields (Y%) of *cis*- and *trans*-cyclopropanocarboxylates against number of runs in the carbene transfer reaction from EDA to styrene catalyzed with $NaAuCl_4$ in the ionic liquid [BMIM] PF_6; (B) comparative Z-average of gold nanoparticles obtained by DLS technique after successive reuses in the cyclopropanation reactions of styrene catalyzed by $NaAuCl_4$ in [BMIM] PF_6.

initial use strongly suggests that the anionic $AuCl_4$ salt likely underwent a reductive transformation in the IL [BMIM] PF_6 during the reaction. UV–vis spectra of the gold-containing [BMIM] PF_6 confirms this fact, with a broad and characteristic absorption band associated with the formation of Au nanoparticles appearing at 520 nm (the typical plasmon absorption resonance band for gold nanoparticles) after initial use (Fig. 9) [50].

We used DLS to evaluate the size of gold particles that formed with $NaAuCl_4$ in the IL [BMIM] PF_6. Analysis of particle size and particle size distribution was carried out on a Malvern Nano Zetasizer analyzer (see Section 2 and Supplementary material). The data obtained reveal that the Z-average particle size for the nanoparticle entities produced after the first two uses was still <10 nm (7.5 and 9.0 nm for gold particles after first and second use, respectively); however, this Z-average increased to 23 nm after a third use (Fig. 8; also see Section 2 and Supplementary material).

At this point, we attempted to identify the chemical species responsible for gold salt reduction by detecting the formation of gold nanoparticles on the basis of DLS. In this case, two different BMIM PF_6 solutions containing $NaAuCl_4$ were treated separately with styrene and ethyldiazoacetate at room temperature under vigorous stirring. The particle size and particle size distribution of these mixtures were analyzed using a Malvern Nano Zetasizer analyzer at different time intervals. These experiments revealed that formation of nanoparticles did not occur after olefin was added (even after 24 h), but gold nanoparticles were formed 2 h after EDA was added (Z-average particle size, 100 nm). Fumarate and maleate esters were detected by GC analysis, whereas a broad and characteristic absorption band associated with the formation of Au nanoparticles at 520 nm in the UV–vis spectrum (the typical plasmon absorption resonance band for gold nanoparticles) was seen [50].

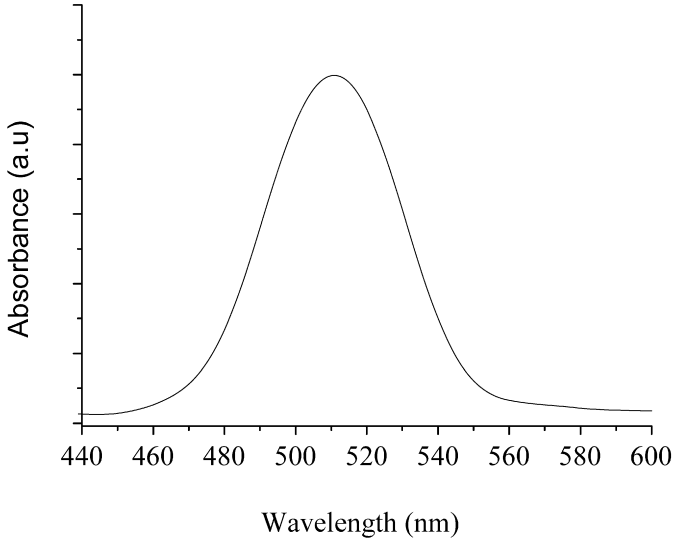


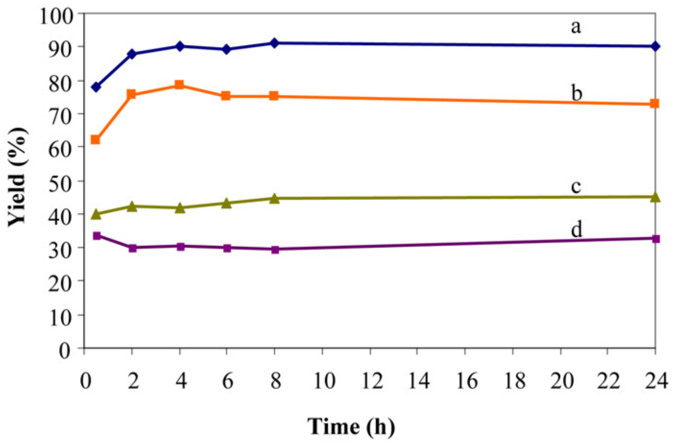
Fig. 9. UV–vis spectrum of $NaAuCl_4$ containing [BMIM] PF_6 after cyclopropanation reaction of styrene with EDA (first use) recorded in $CHCl_3$.

It appears that the increasing nanoparticles size with successive catalyst recyclings may be related to the observed decrease in selectivity toward cyclopropanes. To check this hypothesis, we prepared gold nanoparticles of different sizes (i.e., 8, 22, 79, and 102 nm) following the method by seeding described by Haiss et al. [51] with some modifications. The IL BMIM PF_6 was used as solvent, and $NaBH_4$ was used as reducing agent to form the gold nanoparticles, albeit in the absence of a stabilizing agent. In each case, the [BMIM] PF_6 containing the gold nanoparticles was used in the cyclopropanation reaction of styrene with EDA. The results, shown in Fig. 10, demonstrate a clear dependency of product selectivity on gold particle size for *cis* + *trans*-cyclopropanes and *o*-, *m*-, *p*-aromatic addition products (Figs. 10A and 10B), with the formation of fumarate and maleate esters apparently independent of this parameter (Fig. 10C). The highest yields of cyclopropanes were obtained with the smallest nanoparticles (Fig. 10A), with selectivity remaining high for particle sizes of ∼22 nm and decreasing to approximately 45% and 30% for particle sizes ∼79 and 102 nm, respectively.

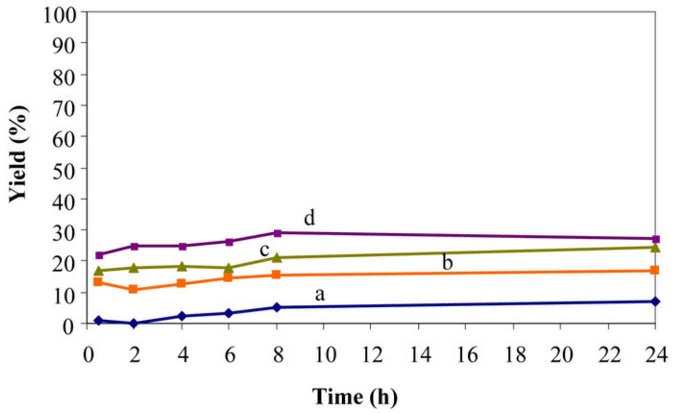
Interestingly, aromatics formed by addition reactions follow the opposite trend with gold particle size, because the selectivity to these products increased with increasing gold particle size (Fig. 10B). This agrees with the fact that the greatest yields of aromatic addition products were obtained in conventional organic solvents (see Table 1), in which the catalyst was rapidly transformed into metal agglomerates during the initial stages of the reaction.

At this point, we reiterate that the instability observed for the IL containing $NaAuCl_4$ (hydrolysis of, e.g., PF_6^-) may facilitate the formation of different gold species that could catalyze the reaction in a nonselective way; making it difficult to correlate the cyclopropane yields with the nanoparticle size in reactions with $NaAuCl_4$ as the catalyst. Finally, the analysis of gold content on the catalyst containing IL ([BMIM] PF_6) revealed no loss of metal from this IL after three reuses.

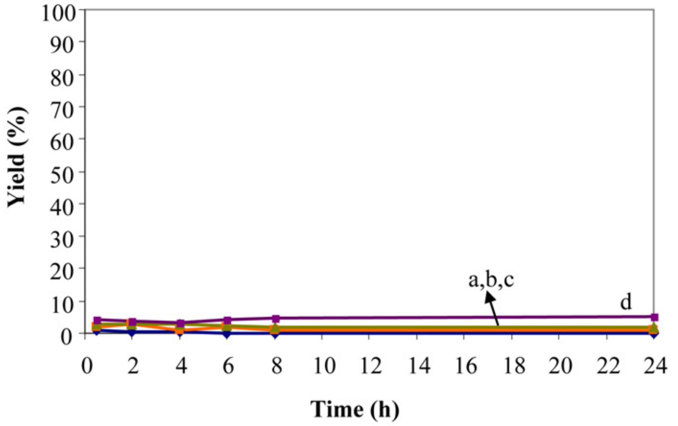
In striking contrast, the greater stability and permanency of $[AuCN_2]^-$ in the IL [BMIM] PF_6 is reflected in the fact that neither loss of activity nor loss of selectivity was seen after three consecutive uses (Fig. 11). In this case, the DLS technique was again used to assess the stability of gold particles that may form with $KAuCN_2$



(A) Yield of *cis* + *trans*-cyclopropanation products versus time

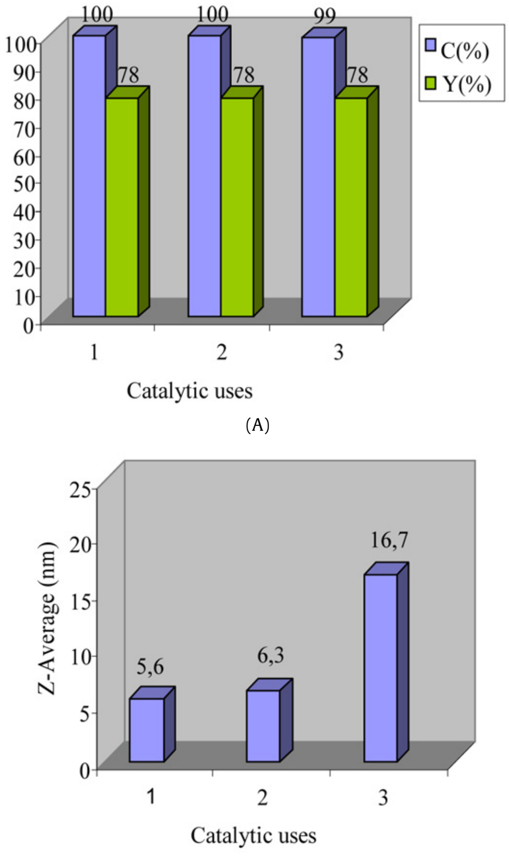


(B) Yield of *o*-, *m*-, *p*-aromatic addition products versus time



(C) Yield of fumarate and maleate esters versus time

Fig. 10. Plots showing the yields of reaction products *versus* time in the cyclopropanation reaction of styrene with EDA catalyzed by gold (0) nanoparticles in the ionic liquid BMIM PF_6. Z-average particle size: (a) 8 nm; (b) 22 nm; (c) 79 nm and (d) 102 nm.



(A)

(B)

Fig. 11. (A) Comparative conversions (C%) and yields (Y%) of *cis*/*trans*-cyclopropanocarboxylates against number of runs in the carbene transfer reaction from EDA to styrene catalyzed with $KAuCN_2$ in the ionic liquid [BMIM] PF6; (B) comparative Z-average of gold nanoparticles obtained by DLS technique after successive reuses in the cyclopropanation reactions of styrene catalyzed by $KAuCN_2$ in [BMIM] PF_6.

in the IL [BMIM] PF_6. The Z-average of the nanoparticle entities produced after initial use was 5.6 nm. These small particles retained almost all of their original size after a second use (6.3 nm) and, in contrast to the previous study, were smaller than 20 nm after a third use (Fig. 11B). The good activity of these small gold nanoparticles is demonstrated by the fact that after three uses the yields to cyclopropanocarboxylates still exceeded those obtained when working with organic solvents. Finally, analysis of gold content revealed that no leaching occurred from the [BMIM] PF_6 IL after three uses.

4. Conclusion

In the present study, ionic gold complexes in different imidazolium ILs were used as recoverable and reusable homogeneous catalysts in the cyclopropanation reaction of alkenes with ethyldiazoacetate to give *cis*- and *trans*-cyclopropanes. The following trends were found: With few exceptions, the *trans*-isomer was the major product of the reaction, and the stability and performance of these gold salts is much higher in ILs than in typical solvents used in this reaction (e.g., 1,2-dichloroethane, CH_2Cl_2, acetonitrile). Nonetheless, salt decomposition also occurred in the IL [BMIM] PF_6, and gold nanoparticles were formed that could be stabilized by the IL, avoiding rapid agglomeration, in contrast to what occurs in conventional solvents, in which large gold metal agglomerates are formed in the first run. This findings has two important implications: Small gold nanoparticles should be active for performing the cyclopropanation reaction, and stable gold metal nanoparticles can be obtained by decomposing the gold salts in determined ILs. The activity of the small gold nanoparticles is demonstrated by the fact that after three uses, the yields to cyclopropanocarboxylates were much larger than those achieved when working with organic solvents. Indeed, the easy workup protocol for conducting gold-catalyzed cyclopropanations facilitates the reaction. Dissolving ionic gold complexes in imidazolium ILs is a very simple strategy for converting a nonrecoverable catalytic system into a reusable and recoverable catalytic system.

Acknowledgments

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Supplementary material

Supplementary material for this article may be found on ScienceDirect, in the online version.

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References

[1] (a) C. Gonzalez-Arellano, A. Abad, A. Corma, H. García, M. Iglesias, F. Sanchez, Angew. Chem. Int. Ed. 46 (2007) 1536;
(b) A. Corma, C. Gonzalez-Arellano, M. Iglesias, S. Perez-Ferreras, F. Sanchez, Synlett 11 (2007) 1771.
[2] (a) S. Ma, S. Yu, Z. Gu, Angew. Chem. Int. Ed. 45 (2006) 200;
(b) V. Mamane, T. Gress, H. Krause, A. Fürstner, J. Am. Chem. Soc. 126 (2004) 8654.
[3] M.H. Suhre, M. Reif, S.F. Kirsch, Org. Lett. 7 (2005) 3925.
[4] A. Corma, C. Gonzalez-Arellano, M. Iglesias, F. Sanchez, J. Catal. 238 (2006) 497;
A. Corma, E. Gutierrez-Puebla, M. Iglesias, A. Monge, S. Perez-Ferreras, F. Sanchez, Adv. Synth. Catal. 348 (2006) 1899.
[5] S. Carrettin, M.C. Blanco, A. Corma, A.S.K. Hashmi, Adv. Synth. Catal. 348 (2006) 1283.
[6] (a) R.A. Widenhoefer, X. Han, Eur. J. Org. Chem. (2006) 4555;
(b) N. Nishima, Y. Yamamoto, Angew. Chem. Int. Ed. 45 (2006) 3314.
[7] (a) Y. Fukuda, K. Utimoto, H. Nozaki, Heterocycles 25 (1987) 297;
(b) T.E. Müller, Tetrahedron Lett. 39 (1998) 5961;
(c) M.R. Luzung, J.P. Markham, F.D. Toste, J. Am. Chem. Soc. 126 (2004) 10858;
(d) D. Kadzimirsz, D. Hildebrandt, K. Merz, G. Dyker, Chem. Commun. (2006) 661.
[8] (a) For recent reviews see: A.S.K. Hashmi, Gold Bull. 37 (2004) 51;
(b) A. Höffmann-Roder, N. Krause, Org. Biomol. Chem. 3 (2005) 387;
(c) A. Arcadi, S. Di Giuseppe, F. Marinelli, E. Rossi, Curr. Org. Chem. 8 (2004) 795.
[9] E. Mizushima, T. Hayashi, M. Tanaka, Org. Lett. 5 (2003) 3349.
[10] A. Corma, P. Concepción, I. Domínguez, V. Fornés, María J. Sabater, J. Catal. 251 (2007) 39.
[11] (a) X. Zhang, A. Corma, Chem. Commun. (2007) 3080;
(b) X. Zhang, A. Corma, Dalton Trans. 3 (2008) 397.
[12] E. Genin, P.-Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genet, V. Michelet, J. Am. Chem. Soc. 128 (2006) 3112.
[13] A. Comas-Vives, C. Gonzalez-Arellano, A. Corma, M. Iglesias, F. Sánchez, J. Am. Chem. Soc. 128 (2006) 4756.
[14] A. Corma, M. Boronat, S. Gonzalez, F. Illas, Chem. Commun. (2007) 3371.
[15] A. Corma, C. Gonzalez-Arellano, M. Iglesias, F. Sanchez, Chem. Commun. (2005) 3451.
[16] (a) A. Corma, C. Gonzalez-Arellano, M. Iglesias, F. Sánchez, Angew. Chem. Int. Ed. 46 (2007) 7820;
(b) A.M. Caporusso, L. Antonella, E. Schiavi, G. Martra, G. Vitulli, P. Salvadori, J. Organomet. Chem. 690 (2005) 1063.
[17] (a) M. Haruta, Catal. Today 36 (1997) 153;
(b) J. Guzman, B.C. Gates, J. Am. Chem. Soc. 126 (2004) 2672;
(c) M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647;
(d) J. Guzman, S. Carrettin, J.C. González-Fierro, Y. Hao, B.C. Gates, A. Corma, Angew. Chem. Int. Ed. 44 (2005) 4778;
(e) S. Biella, M. Rossi, Chem. Commun. (2003) 378;
(f) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Chem. Commun. (2002) 696;
M.D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D.I. Enache, A.F. Carley, G.A. Attard, G.J. Hutchings, F. King, E. Hugh Stitt, P. Johnston, K. Griffin, C.J. Kiely, Nature 437 (2005) 1132.
[18] (a) Y. Ito, M. Sawamura, T. Hayashi, J. Am. Chem. Soc. 108 (1986) 6405;
(b) C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, Chem. Commun. (2005) 3451.
[19] A.S.K. Hashmi, Angew. Chem. Int. Ed. 44 (2005) 6990;
L. Zhang, S. Wang, J. Am. Chem. Soc. 128 (2006) 1442.
[20] M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911–933.
[21] H.N.C. Wong, M.Y. Hon, C.W. Tse, Y.C. Yip, J. Tanko, T. Hudlicky, Chem. Rev. 89 (1989) 165.
[22] M.P. Doyle, McKervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides, Wiley, New York, 1998.
[23] M.R. Fructos, T.R. Belderrain, M.C. Nicasio, S.P. Nolan, H. Kaur, M.M. Diaz-Requejo, P.J. Pérez, J. Am. Chem. Soc. 126 (2004) 10846.
[24] A.J. DelMonte, E.D. Dowdy, D.J. Watson, in: Organometallics in Process Chemistry, in: Topics in Organometallic Chemistry, vol. 6, Springer-Verlag, 2004, pp. 97–122.
[25] G. Maas, Chem. Soc. Rev. 33 (2004) 183.
[26] K. Miki, K. Ohe, S. Uemura, J. Org. Chem. 68 (2003) 8505.
[27] J.S. Yadav, B.V.S. Reddy, P. Narayana Reddy, Adv. Synth. Catal. 346 (2004) 53.
[28] M.R. Fructos, T.R. Belderrain, P. de Fremont, N.M. Scott, S.P. Nolan, M.M. Diaz-Requejo, P.J. Pérez, Angew. Chem. Int. Ed. 44 (2005) 5284.
[29] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, J. Chem. Soc. Chem. Commun. (1994) 801.
[30] T. Welton, Chem. Rev. 99 (1999) 2071.
[31] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
[32] R. Sheldon, Chem. Commun. (2001) 2399.
[33] C.M. Gordon, Appl. Catal. A 222 (2001) 101.
[34] R. Giernoth, Top. Curr. Chem. 276 (2007) 1.
[35] R.D. Rogers, K.R. Sheldon, J. Am. Chem. Soc. 125 (2003) 7480.
[36] N.V. Plechkova, K.R. Seddon, in: P. Tundo, A. Perosa, F. Zecchini (Eds.), Methods and Reagents for Green Chemistry, Wiley, Hoboken, 2007.
[37] M. Maase, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, second ed., Wiley–VCH, Weinheim, 2008, pp. 663–687.
[38] N.V. Plechkova, K.R. Seddon, Chem. Soc. Rev. 37 (2008) 123.
[39] H. Zao, S.V. Malhotra, Aldrichim. Acta 35 (2002) 75.
[40] (a) J. Durand, E. Teuma, F. Malbosc, Y. Kihn, M. Gómez, Catal. Commun. 9 (2008) 273;
(b) J. Kraemer, E. Redel, R. Thomann, C. Janiak, Organometallics 27 (2008) 1976;
(c) X. Yang, Z. Fei, D. Zhao, W.H. Ang, Y. Li, P.J. Dison, Inorg. Chem. 47 (2008) 3292;
(d) G. Machado, J.D. Scholten, T. da Vargas, S.R. Teixeira, L.H. Ronchi, J. Dupont, Int. J. Nanotechnol. 4 (2007) 541;
(e) C. Vincenzo, N. Angelo, A. Monopoli, A. Damascelli, I. Eliana, N. Cioffi, J. Organomet. Chem. 692 (2007) 4397;
(f) M. Pedro, J. Dupont, Chem. Eur. J. 13 (2006) 32;
(g) D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed. 44 (2005) 7852;
(h) M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, Angew. Chem. Int. Ed. 43 (2004) 4988;
(i) H. Itoh, K. Naka, Y. Chujo, J. Am. Chem. Soc. 126 (2004) 3026.
[41] (a) D.E. Koppel, J. Chem. Phys. 57 (1972) 4814;
(b) B.J. Frisken, Appl. Opt. 40 (2001) 4087;
(c) P.A. Hassan, S.K. Kulshreshtha, J. Colloid Interface Sci. 300 (2006) 744;
(d) E.R. Sadiku, R.D. Anderson, J. Appl. Polym. Sci. 102 (2006) 166.
[42] G.C. Bond, C. Louis, D.T. Thompson, in: G. Hutchings (Ed.), Catalysis by Gold, in: Catalytic Science Series, vol. 6, Imperial College Press, London, 2006.
[43] J.R. van Wazer, Phosphorous and Its Compounds, vol. 1, Wiley, New York, 1958.
[44] G.S. Fonseca, A.P. Umpierre, P.F.P. Fichtner, S.R. Teixeira, J. Dupont, Chem. Eur. J. 9 (2003) 3263.
[45] X. Liu, et al., Appl. Catal. A 239 (2003) 279–286;
H.U. Blaser, A. Baiker, R. Prins, in: J.M. Fraile, B. García, J.I. García, J.A. Mayoral, F. Figueras (Eds.), Heterogeneous Catalysis and Fine Chemicals, IV, in: Studies in Surface Science and Catalysis, 1997, p. 571.
[46] A.V. Plakhonyk, L. Ernt, R. Schmutzler, J. Fluorine Chem. 126 (2005) 27.
[47] K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (12) (2000) 2275.
[48] L. Xu, W. Chen, J. Xiao, Organometallics 19 (2000) 1123.
[49] Z.L. Li, T.H. Wu, Z.J. Niu, W. Huang, H.D. Nie, Electrochem. Commun. 6 (2004) 44.
[50] (a) U. Kreibig, M. Vomer, Optical Properties of Metal Clusters, Springer-Verlag, Heidelberg, 1995;
(b) G.P. Mitchell, C.A. Mirkin, R.L. Letsinger, J. Am. Chem. Soc. 121 (1999) 8122;
(c) Y. Voloktitin, J. Sinzing, L.J. Jong, G. Schmid, M.N. Vargaftik, I.I. Moiseev, Nature 384 (1996) 621;
(d) G. Schmid, Chem. Rev. 92 (1992) 1709;
(e) M. Kanehara, E. Kodzuka, T. Tenarishi, J. Am. Chem. Soc. 128 (2006) 13084.
[51] W. Haiss, N.T.K. Thanh, J. Aveyard, D.G. Fernig, Anal. Chem. 79 (2007) 4215.