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Alkyne Hydroarylation in Ionic Liquids Catalyzed by Palladium(II) Complexes

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The efficiency of dicarbene palladium(II) complexes and of simple palladium(II) acetate as catalysts for alkyne hydroarylation under liquid-liquid biphasic conditions involving an ionic liquid as the catalyst-containing phase is investigated. The results obtained under these conditions, both in terms of activity and selectivity, are compared with those previously obtained under homogeneous conditions. The catalytic efficiency of the systems is found to be markedly dependent on the nature of the anion of the ionic liquid. Suitable anions are found to significantly improve the catalytic performance in comparison to homogeneous conditions. Preliminary investigations on the recyclability of the system as well as the on advantages of using an acidic ionic liquid are also carried out.

Introduction

lonic liquids have undergone a tremendous development during the past decade, and this development is still ongoing. Their applications range from solvents for reactions in chemical synthesis to media for electrochemical processes, and from active phases for extraction and separation techniques to additives for novel composite materials.^[1] Reactions catalyzed by acids (Brønsted- or Lewis-type) occupy a special place among the many reactions investigated in ionic liquids, because such reactions generally proceed through cationic intermediates that are expected to be stabilized by an ionic liquid, thereby leading to

substantial rate enhancements. Indeed, these reactions were among the earliest to be investigated in these solvents and numerous examples are known to date.^[2] For the same reason, reactions that require a cationic metal complex as catalyst have also been intensively studied in ionic liquid media, because these solvents favor the generation of the catalytically active cationic species through the dissociation of anionic ligands from the catalyst precursor.^[2, 3]

We have been interested for some time in the use of ionic liquids as reaction media for cationic complex catalysts, for use in silane alcoholysis.^[4] Herein, we report on the application of ionic liquids as media for another reaction that is the object of intense studies by our group. We have recently shown that chelating *N*-heterocyclic dicarbene^[5] palladium(II) complexes such as 1 (Scheme 1; where X is an anionic ligand such as halide, carboxylate, tetrafluoroborate, or triflate) are efficient catalysts for the hydroarylation of alkynes with simple arenes: depending on the reaction conditions, a product of formal trans-hydroarylation of the triple bond A or a double-insertion product **B** can be obtained.^[6] The optimized reaction conditions require that the catalyst bears weakly coordinating anionic ligands, because the catalytically active species is a cationic complex. Furthermore, the reaction involves a large amount of a strong acid (trifluoroacetic, triflic, or tetrafluoroboric acid) as



Scheme 1. Alkyne hydroarylation catalyzed by chelating dicarbene palladium(II) complexes.

reaction promoter, thus decreasing the cleanliness of the process and its technological applicability. Hence, we reasoned that the use of ionic liquids as solvents for this reaction could have at least two advantageous aspects: (1) ionic liquids should facilitate the dissociation of anionic ligands from the metal complex that leads to the formation of the catalytically active species; and (2) ionic liquids should preferentially dissolve the strong acid promoter, allowing its separation and recycling. Incidentally, ionic liquids have been previously employed as media for alkyne hydroarylations with alternative catalytic systems and were found to dramatically improve the catalytic performance.^[7] Based on the above, we set out to evaluate the catalytic efficiency of dicarbene palladium(II) complexes in alkyne hydroarylation under liquid-liquid biphasic conditions involving an ionic liquid as catalyst-containing phase.

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Results and Discussion

We started our investigation by studying the reaction between pentamethylbenzene and ethyl propiolate in various commercial ionic liquids (Scheme 2), adopting the reaction conditions



Scheme 2. lonic liquids employed in this study.

previously optimized by us, which imply the use of an equimolar amount of arene and alkyne, 0.1 mol% catalyst, and room temperature.^[6] The solvent for the reaction was a three-component system comprising trifluoroacetic acid (1 equiv with respect to the reagents), ionic liquid (3 mL), and 1,2-dichloroethane (necessary to dissolve the arene) in an amount required to reach an arene concentration of 2.1 mol L^{-1} , that is, the value that we previously found to be optimal for this type of reaction.^[6b] We checked initially that a strong acid was indeed needed for the reaction even in the presence of an ionic liquid by performing several blank tests in [BuMe₃N][NTf₂] or [BMMIM][NTf₂], using complex **1a** in the absence of trifluoroacetic acid. The reaction did not proceed at all, neither at room temperature nor at 50 °C.

Analysis of the conversion curves obtained with trifluoroacetic acid in the different ionic liquids clearly highlighted the fact that the efficiency of the catalytic system was strongly dependent on the nature of the anion of the ionic liquid. In fact, in ionic liquids with the same anion but different cations the system presented virtually the same activity (Figure 1). On the other hand, by changing the anion (Figure 2) the activity varied markedly and was found to be either higher or lower than that recorded without ionic liquid.

Considering the fact that cationic metal species are invoked as intermediates in the catalytic cycle for the Fujiwara reaction,^[8] it is not entirely surprising that only the anion of the ionic liquid influences the catalytic activity of the system, presumably upon interaction with the metal center. Although the anions of most commercially available ionic liquids are usually defined as noncoordinating, it has been demonstrated that they can interact with cationic metal centers through coordination or by formation of intimate ion pairs.^[9] Indeed, the activity of the system decreased as a function of the coordinating ability of the different anions in the order NTf₂⁻ > PF₆⁻ > BF₄⁻ > OTf⁻. The ionic liquids with the bis(trifluoromethylsulfonyl)imide (NTf₂⁻) anion, which is the least-coordinating one,



Figure 1. Arene conversion (%) vs. time for the hydroarylation reaction of pentamethylbenzene and ethyl propiolate catalyzed by complex **1 a** in different ionic liquids: effect of the cation of the ionic liquid on the efficiency of the reaction. Without ionic liquid (\Box); [BMMIM][BF4] (+); [BMIM][BF4] (*); [MeOct3N][NTf2] (\odot); [BuMe3N][NTf2] (\blacksquare); [BMMIM][NTf2] (\triangle).



Figure 2. Arene conversion (%) vs. time for the hydroarylation reaction of pentamethylbenzene and ethyl propiolate catalyzed by complex **1 a** in different ionic liquids: effect of the anion of the ionic liquid on the efficiency of the reaction. Without ionic liquid (\Box); [BMMIM][BF4] (+); [BMMIM][NTf2] (Δ); [BMMIM][PF6] (**A**); [BMMIM][OTF] (**●**).

showed the best conversion, while the ionic liquid with triflate anion (OTf⁻) showed the worst conversion. On the other hand, the selectivity of the system towards the *trans*-hydroarylation product after 48 h was not influenced by the employed ionic liquid and remained almost constant in the range 78–84%; the rest of the converted reagents going into the double-insertion product **B** (Scheme 1). These results highlight that, by a proper choice of the ionic liquid, it is possible to significantly enhance the catalytic efficiency of the system.

By using simple palladium(II) acetate in the ionic liquid [BMMIM][NTf₂] the catalytic efficiency was higher than in the absence of the ionic liquid (Figure 3); this is not surprising when considering that in both cases cationic species are postulated as catalytic intermediates. However, the conversion enhancement was much more pronounced when using catalyst **1 a** (Figure 1). This difference may be explained by consid-

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Figure 3. Enhancement of catalytic activity through the use of ionic liquid $[BMMIM][NTf_2]$ with catalyst 1 a or Pd(OAc)₂; [HTFA] = 2.1 M.

ering that whereas in the case of simple $Pd(OAc)_2$ monocationic species are invoked as catalytically competent species,^[8] in the case of complex **1a** and related complexes experimental evidence favors dicationic complexes as the species responsible for the observed catalytic activity.^[6b] On the other hand, the reactivity trend exhibited by $Pd(OAc)_2$ in the different ionic liquids is the same observed with the dicarbene complex: performing the reaction in [MeOct₃N][NTf₂] resulted in a conversion comparable to that obtained with [BMMIM][NTf₂] (42% vs. 48% after 23 h), whereas much lower conversions were obtained in [BMMIM][BF₄] (18% conversion after 23 h).

Subsequently, ionic liquid [BuMe₃N][NTf₂] was used to compare the activity and selectivity of the system with different Brønsted-acid co-catalysts, such as triflic or tetrafluoroboric acid, together with palladium dicarbene complexes with weakly coordinating anionic ligands derived from the same acids. These catalytic systems were previously investigated by us in conventional organic solvents and were found to exhibit widely different catalytic activities as well as reaction selectivities, depending on the nature of the employed acid.^[6c] In particular, the use of HBF₄ caused preferred formation of product **B** (Scheme 1).

The catalysts were prepared in situ by reacting complex 1b with two equivalents of the silver salt bearing as anion the conjugated base of the employed acid (AgBF₄ in the case of HBF₄ and AgOTf in the case of HOTf). The resulting conversion curves have been expressed both as a function of the alkyne consumption (Figure 4) and of the arene consumption (Figure 5), because whenever significant amounts of product B are formed the alkyne becomes the limiting reagent. The activity of the catalytic system in the ionic liquid was found to be influenced by the type of acid and to follow the order HTFA pproxHOTf < HBF₄. Acids stronger than HTFA could be in principle expected to perform better, because it is generally accepted that the rate-determining step of the catalytic cycle is the protonolysis of the Pd-vinyl intermediate.^[8] On the other hand, in the absence of ionic liquid we previously observed that the relative reactivity recorded with the various acids is not directly proportional to their acidic strength; for example HBF₄ (pKa



Figure 4. Alkyne conversion curves (%) vs. time for the hydroarylation reaction between pentamethylbenzene and ethyl propiolate in ionic liquid [BuMe₃N][NTf₂] using different acids/anionic ligands.



Figure 5. Arene conversion curves (%) vs. time for the hydroarylation reaction between pentamethylbenzene and ethyl propiolate in ionic liquid [BuMe₃N][NTf₂] using different acids/anionic ligands.

-4.9) performed better than HOTf (pKa -14).^[6c] We have interpreted this observation as a balance between the strength of the acid and the coordinating ability of its conjugated base, because BF₄⁻ is a less-coordinating anion than OTf⁻.

The presence of the ionic liquid further complicates the picture. The ionic liquid increases on the one hand the reaction rate in the case of catalyst **1a** with trifluoroacetic acid, as outlined above. On the other hand, a marked reduction in the reaction rate compared to homogeneous conditions is seen in the case of the **1b**/AgOTf/HOTf system, whose performance in the ionic liquid is almost the same as **1a**/HTFA despite the widely different strength of the two acids (pKa –0.25 vs. pKa –14). Finally, the activity of the system **1b**/AgBF₄/HBF₄ is nearly the same with or without ionic liquid.

Looking at the different reaction selectivities recorded in the ionic liquid with the three acids (Table 1), in HTFA the system is selective towards the *trans*-hydroarylation product **A**, while in HBF₄ and HOTf product **B** predominates. This type of selectivity reflects the observations in the absence of ionic liquid,

Table 1. Selectivity at 23 h for the reaction of pentamethylbenzene and ethyl propiolate catalyzed by complex 1 a or 1 b/2 AgX using different HX acids, both in the presence or absence of ionic liquid (IL) [BuMe₃N][NTf₂].

Yield A	[%] B	Arene conversion [%]	Alkyne conversion [%]
45	9	54	63
20	3	23	26
15	40	56	97
7	43	50	93
13	26	40	67
45	0	65	72
	Yield A 45 20 15 7 13 45	Yield [%] A B 45 9 20 3 15 40 7 43 13 26 45 0	Yield [%] Arene conversion [%] 45 9 54 20 3 23 15 40 56 7 43 50 13 26 40 45 0 65

[a] Reaction performed with complex **1a**. [b] Additional by-products stemming from double-bond isomerization and ester hydrolysis are formed in this case, see Ref. [6].

except for HOTf, whose chemoselectivity is inverted in the ionic liquid. Furthermore, using HOTf in the ionic liquid, side reactions such as hydrolysis of the ester function and double bond isomerization, which negatively affected the selectivity in organic solvents, were found to be mini-

These experimental findings can be interpreted in the following terms. The enhanced activity recorded in the ionic liquid with the system **1**a/HTFA, as well as the inverted reaction selectivity observed with **1**b/AgOTf/HOTf

are related to the weakening

effect of the ionic liquid on the interaction between the palladium centre and the anionic li-

mized.

using one equivalent of HTFA as the acid promoter. The results are reported in Table 2.

Although the reported conversions may appear modest, they are fully comparable with those previously obtained in the homogeneous phase with four equivalents of acid promoter (instead of one equivalent as in the present case).^[6c] Consequently, it can be safely stated that the catalytic system in the ionic liquid exhibits a superior performance in comparison to the homogeneous system.

We have also evaluated the possibility to use the ionic liquid phase for recovering and recycling the complete catalytic system, that is, the palladium catalyst and the acid employed as co-catalyst. For this purpose, a reaction was run using complex **1a** with HTFA and ionic liquid [BuMe₃N][NTf₂]. After 48 h

Table 2. Hydroarylation reactions catalyzed by complex 1 a using HTFA and the ionic liquid [BuMe ₃ N][NTf ₂]. ^[a]					
Arene	Alkyne	Product	Yield [%]	Arene conversion ^[b]	
	HCO ₂ Et	H H CO ₂ Et	45	54 (63) ^[c]	
	HCO ₂ Et	H H CO ₂ Et	10	13 (16) ^[c]	
	HCO2Et	H H CO ₂ Et	30	37 (44) ^[c]	
1 1 1 1	PhCO ₂ Et	Ph H CO ₂ Et	8	8 (8)	
	H-—Ph	Ph H H	10	10 (10)	

[a] Yields and conversions determined at 23 h. [b] Alkyne conversion in parentheses. [c] An additional product stemming from double insertion of alkyne is formed in this case.

gands, which facilitates formation of the catalytically competent species (in the case of TFA⁻) and relieves the coordination sphere of the metal thereby favoring the coordination of a second molecule of alkyne to give product **B** (in the case of OTf⁻). The system **1 b**/AgBF₄/HBF₄, in which the anionic ligands interact only very weakly with the metal center, remains instead unaffected. On the other hand, the decreased activity of the system **1 b**/AgOTf/HOTf together with the lower incidence of unwanted acid-catalyzed side reactions with the same system indicates that the acidic strength of triflic acid in the ionic liquid is diminished as a consequence of the greater solvation of the protons by the anions of the ionic liquid.^[10] These solvation effects do not affect the performance of less strong acids such as HTFA or HBF₄.

On the basis of the above, it can be inferred that use of an ionic liquid with a suitable noncoordinating anion as the catalyst-containing phase allows to operate the hydroarylation reaction using a lower amount of a weaker acid compared to homogeneous conditions. We have proved this inference by subjecting different arene and alkyne substrates to hydroarylation an arene conversion of 72% was reached; the ionic liquid phase was separated by simple extraction of the products and of the unreacted reagents with n-pentane. Unfortunately though, with this procedure a large amount of acid (ca. 60% of the initially employed amount) was removed from the ionic liquid, whereas ICP-AAS analysis of the palladium content in the combined organic phases demonstrated that 95% of palladium was retained in the ionic liquid phase. We checked the catalytic efficiency of the catalyst containing phase after addition of fresh reagents as well as of acid to restore the initial acid concentration. Only a moderate decrease (ca. 10%) in the arene conversion was registered, which in the light of the very low level of palladium leaching into the organic phase could be the consequence of some degree of catalyst decomposition in the ionic liquid phase. The selectivity of the system remained constant, around 80% towards product A in both cycles. Thus, upon using liquid-liquid biphasic conditions involving an ionic liquid as catalyst-containing phase, a catalytic system is obtained which allows to efficiently recover and recycle the palladium catalyst but not the acid co-catalyst, which is lost to a large extent during extraction. Experiments performed with other acids such as triflic acid pointed out that also in this case substantial acid leaching from the ionic liquid phase into the organic phase takes place.

In order to overcome this problem we envisaged to avoid the need for an external acid, and consequently we decided to test an intrinsically acidic ionic liquid such as [BIM3SH][NTf₂] (Scheme 3), which was synthesized by reaction of the known zwitterionic compound BIM3S^[11] with HNTf₂. We chose HNTf₂ as the protonating acid in order to obtain an ionic liquid with the NTf₂⁻ counteranion, which gave the best results in the previously performed catalytic tests.



Scheme 3. Acid ionic liquid [BMI3SH][NTf₂].

Preliminary hydroarylation experiments performed in this protic ionic liquid (1 equiv with respect to the reagents, as in the previous tests) with catalyst **1a** indicate that this system is indeed catalytically active, even in the absence of an added external acid. However, the catalytic efficiency is moderate both at room temperature (14% of conversion after 48 h) and at 50 °C (23% of conversion after 48 h; Figure 6). Moreover the system is not selective; forming almost identical quantities of both the *trans*-hydroarylation product **A** and the double insertion product **B**.



Figure 6. Arene conversion curves (%) vs. time for the hydroarylation reaction between pentamethylbenzene and ethyl propiolate, catalyzed by complex 1 a, in the acidic ionic liquid [BIM3SH][NTf₂] compared to [BuMe₃N]-[NTf₂].

Conclusions

lonic liquids can be employed as reaction media for alkyne hydroarylations catalyzed by palladium(II) complexes. The nature of the anion of the ionic liquid markedly influences the catalytic efficiency, and best results were obtained with the $\rm NTf_2^-$ anion. Such ionic liquids substantially increase the reaction

rate when weaker acids having more strongly coordinating conjugated bases are employed as reaction promoters, thereby allowing to operate under milder conditions. Through the use of ionic liquids as the catalyst-containing phase, the palladium catalyst can be efficiently separated from the reaction mixture and recycled, whereas substantial amounts of the acid promoter are lost into the reagents and products phase. Work currently in progress aims at developing alternative intrinsically acidic ionic liquids in order to obtain a catalytic system that is fully recoverable and recyclable.

Experimental Section

General remarks: All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or dinitrogen. The reagents were purchased from Aldrich as high-purity products and generally used as-received. Compounds $1 a^{[6c]}$ and $1 b^{[6a]}$ and BIM3S^[11a] were prepared according to literature procedures. All solvents were used as-received as technical grade solvents. NMR spectra were recorded on a Bruker Avance 300 MHz (300.1 MHz for ¹H and 75.5 MHz for ¹³C); chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals.

Synthesis of the ionic liquid [BIM3SH][NTf₂]: BIM3S (2.82 g, 6.1 mmol) and bis(trifluoromethanesulfonyl)imide (1.71 g, 7.9 mmol) where stirred at 50 °C for 6 h, during which time both solids melted, giving the 3-butyl-1-(butyl-4-sulfonyl)imidazolium bis(trifluoromethylsulfonyl)imide [BIM3SH][NTf₂]. The IL phase was then washed several times with toluene and diethyl ether and finally dried in vacuum. The product purity was confirmed via NMR as well as via titration with standard NaOH.

General procedure for the catalytic tests: Pentamethylbenzene (13.2 mmol), the palladium(II) complex **1a** or **1b** (0.013 mmol) and the silver salt (0.026 mmol, AgOTf when HOTf was used, AgBF₄ for HBF₄; no silver salt was used with complex **1a**) were placed in a 100 mL round-bottomed flask, previously evacuated and filled with argon. The ionic liquid (3 mL), the acid (13.2 mmol), and 1,2-di-chloroethane (1 mL when HTFA was used, 0.8 mL for HOTf, 0.6 mL for HBF4) were then added and the resulting solution was stirred at 25 °C for 5 min. Finally ethyl propiolate (13.2 mmol) was added and the reaction mixture was further stirred at 25 °C for the times indicated in the figures. Portions of the solution (0.2 mL) were drawn off from the reaction mixture and analyzed by ¹H NMR or GC-MS.

In the recycling test with the ionic liquid $[BuMe_3N][NTf_2]$ the products and the unreacted starting materials were extracted from the ionic liquid with *n*-pentane (4×10 mL). The extent of palladium leaching was determined by digestion in 6 mL hot aqua regia of the residue obtained evaporating the volatiles from the organic phase. The resulting solution was diluted to 100 mL with water and its palladium content was determined by ICP-AAS.

General procedure for the catalytic tests reported in Figure 6: Pentamethylbenzene (4.32 mmol) and the palladium(II) complex **1a** (4.3 µmol) were placed in a 100 mL round-bottomed flask, previously evacuated and filled with argon. The ionic liquid [BMI3SH]-[NTf₂] (4.32 mmol) and 1,2-dichloroethane (0.33 mL) were then added and the resulting mixture was stirred at 25 °C for 5 min. Finally ethyl propiolate (4.32 mmol) was added and the reaction mixture was further stirred at 25 °C or 50 °C for the times indicated in the figure. Portions of the solution (0.2 mL) were drawn off from the reaction mixture and analyzed by ¹H NMR.

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