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A water-soluble pyridyl-triazole ligand for aqueous phase palladium catalyzed Suzuki-Miyaura coupling*

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An environmentally friendly water-soluble ligand has been prepared by "clicking" 2-(azidomethyl)pyridine with but-3-ynyl sodium sulphate. In situ combination of the new ligand with $[Pd(\eta^3-C_3H_5)Cl]_2$ (Pd : ligand = 1:1) provides a highly active catalytic system for the Suzuki–Miyaura reaction. Coupling of phenylboronic acid with a variety of aryl or heteroaryl bromides is carried out at catalyst loadings of 0.01% or lower under conventional heating. The aqueous catalytic phase may be used three times without loss of activity.

Introduction The Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acids is one of the most powerful and versatile methods for the synthesis of biaryls.1 Usually the reaction is carried out in an organic solvent employing a transition metalcatalyst and a base. Water is an attractive alternative to the traditional organic solvents employed in S-M coupling because it is inexpensive, nontoxic and non-flammable; furthermore, a catalytic process carried out in water allows an effortless recovery of the insoluble reaction products and a prompt recycle of catalyst. Water was first employed as the solvent for S-M coupling by Beletskaya² in 1989 and nowadays water-soluble catalysts are increasingly employed either in water alone or in water-organic solvent biphasic mixtures. The advancement of the research in this field has been the topic of a number of reviews.3,4

OSO₃Na

Scheme 1 Synthesis of the water-soluble pyridyl-triazolyl ligand 1

Besides employing green reaction media, the use of catalysts and ligands prepared according to atom economical reactions is advisable in order to improve the sustainability of a process. Recently, taking advantage of the copper-catalyzed azide-alkyne [3 + 2] cyclization (see Scheme 1), we have synthesized a small library of N-N or N-S ligands which were successfully employed in conventional S-M reactions.5 The ultimate aim of our studies is to take advantage of the modular nature of the copper-catalyzed Huisgen reaction in order to finely tune the electronic and steric properties of N-donor ligands. As an extension of this work we were intrigued by the possibility of modifying one of the most catalytically active triazolyl ligands to make it watersoluble. Accordingly, we wish to report herein the synthesis of the new ligand 1 and the study of its activity in palladium catalyzed S-M coupling.

Results and discussion

Ligand 1 is obtained in high yield by coupling 2-(azidomethyl) pyridine with but-3-ynyl sodium sulfate in t-BuOH using Cu(OAc)₂ (see Scheme 1) according to the protocol developed by Zhu⁶ which does not require the presence of a reductant. 1 displays good solubility in water, methanol and DMSO, and its identity was confirmed by elemental analysis, the ESI-MS spectrum in the negative mode and ¹H and ¹³C NMR spectroscopy; the relevant data (see the Experimental and the ESI[†]) are in close agreement with those of other pyridyl-triazole ligands and do not deserve particular comments.5b,6

In order to develop a very simple and general protocol for the reaction, we devised to prepare the catalyst *in situ* by combining 1 and a suitable source of palladium in water. Early experiments carried out employing PdCl₂ or Na₂PdCl₄ led to not well reproducible catalytic systems, thus we settled to prepare the catalyst by mixing a methanol solution of allyl complex [Pd(η^3 - C_3H_5 Cl]₂ with an aqueous solution of 1 (Pd/1 = 1:1). This approach was indeed successful allowing to prepare stock



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solutions of the catalytic system which showed to be shelf-stable for weeks.

For a preliminary assessment of the catalyst efficiency and to optimize the reaction conditions, we initially investigated the reaction of 4-bromoacetophenone with phenylboronic acid (see Table 1).

The experiments were carried out in the presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst (PTC) in order to ensure a good migration of the organic substrate into the aqueous phase^{3b} employing K_2CO_3 as the base. At 110 °C the reaction can be carried out with catalyst loadings as low as 0.001 mol% giving the expected coupling product in almost quantitative yield by only two hours (entry 1 of Table 1). The high catalytic efficiency of **1** is demonstrated by the fact that almost total substrate conversion is obtained in two hours even when the reaction temperature is lowered to 70 °C (entries 2 and 3). On the other hand, when the reaction temperature is further lowered to 50 °C a sudden significant decrease of the reaction rate is observed. It should be pointed out that the reduced yield is not due to catalyst deactivation since the reaction conversion can be increased by increasing the reaction time (entry 5).

The influence of the presence of TBAB is highlighted by data in entries 6–8 of Table 1. While at 110 °C the reaction goes to completion even when no phase transfer catalyst is present, at lower temperatures a small, but significant decrease of the reaction rate is observed in the absence of the ammonium salt.

To better understand the influence played by the anion of the quaternary ammonium salt, experiments were carried out employing tetrabutylammonium chloride (TBAC) or tetrabutylammonium acetate (TBAAc) (entries 9 and 10 of Table 1)

Table 1	Influence	of the	temperature	on	the	coupling	of	phenylboronic	acid
with 4-bro	omoacetop	bhenon	e ^a						



Entry	$T(^{\circ}C)$	PTC (mmol)	Conv. ^b (%)	$\operatorname{Yield}^{b,c}(\%)$	TON ^d
1	110	TDAD (2)	00	00 (02)	10 ⁵
2	90	TBAB (3)	99	97 97	10^{5}
3	70	TBAB (3)	99	97	10^{5}
4	50	TBAB (3)	5	5	$5 imes 10^3$
5	50^e	TBAB (3)	25	25	$2.5 imes10^4$
6	110	_	99	90	10^5
7	90	—	88	77	$8.8 imes10^4$
8	70	_	67	62	$6.7 imes10^4$
9	50^e	TBAC (3)	45	40	$4.5 imes10^4$
10	50^e	TBAAc (3)	29	24	$2.9 imes10^4$

^{*a*} Under aerobic conditions: Pd/substrate = 1 : 100 000; 4-bromoacetophenone: 2.0 mmol; phenylboronic acid: 2.4 mmol; K_2CO_3 : 3.0 mmol; 10 mL of H₂O; reaction time = 2 h. ^{*b*} By GLC with *n*-undecane as internal standard. ^{*c*} In parentheses: isolated yield. ^{*d*} TON: turnover number = mol of substrate converted/mol of catalyst. ^{*e*} Reaction time = 18 h.

 Table 2
 Catalyst recycle experiments^a

Catalytic run	$\operatorname{Conv.}^{b}(\%)$	$\operatorname{Yield}^{b}(\%)$
1	99	99
2	99	99
3	95	76
4	40	26

^{*a*} Under aerobic conditions: Pd/substrate = 1 : 100 000; 4-bromoacetophenone: 2.0 mmol; phenylboronic acid: 2.4 mmol; K₂CO₃: 3.0 mmol; TBAB: 3.0 mmol; 10 mL of H₂O; reaction time = 2 h; T = 110 °C. ^{*b*} By GLC using *n*-undecane as internal standard.

instead of TBAB. While TBAAc appears almost equivalent to TBAB, the chloride appears significantly more effective under the same reaction conditions, in agreement with previous results obtained by us employing other triazolyl-based ligands in palladium catalyzed S–M reaction.^{5c} Even if these results reveal that TBAC is more effective than TBAB, in all the following experiments we preferred to employ this latter owing to its inexpensiveness which makes the process more cost-effective.

The use of water as the solvent in catalysis offers as additional advantage an effortless catalyst recycle and a prompt recovery of the products either by filtration or by extraction with an appropriate organic solvent. To verify if at the end of the reaction the aqueous phase is still catalytically active, we performed some catalyst recycle experiments using the model 4bromoacetophenone-phenylboronic acid coupling. The product was isolated by simple filtration of the reaction mixture, then fresh substrates and base were added to the recovered aqueous phase for another catalytic run. According to the data gathered in Table 2, the catalyst can be used in three consecutive reactions (two recycles) without significant loss of efficiency; only when the catalytically active aqueous phase is employed in a fourth experiment a substantial decrease in substrate conversion is observed.

In this connection, it is worth to note that the raw product recovered by filtration contains about 10% of TBAB. Since during the recycling experiments the TBAB level in the aqueous phase was not restored, we are brought to believe that the decrease in catalytic activity after the second recycle is due to loss of the phase transfer agent combined with accumulation of the saline by-products. Most importantly, the experiments showed that, our catalytic system maintains its efficiency for three consecutive catalytic runs. This is a reasonably good result which in our opinion suggests that the catalyst is actually working in the aqueous phase.⁷

With optimized reaction conditions in hand, we tested the catalyst system with a variety of aryl bromides having different steric and electronic parameters (Table 3).

As expected the electron-neutral non-activated bromobenzene is less reactive than 4-bromoacetophenone, the reaction rate being approximately one third that of the model substrate under the same reaction conditions (compare entry 1 in Table 3 with entry 3 in Table 1); nevertheless, complete substrate conversion can be obtained either by increasing the reaction temperature to 90 °C or by decreasing the substrate to palladium molar ratio to 10 000 : 1. Using this catalyst loading,

Table 3Scope of the catalyst^a

$\langle \rangle$	──B(OH) ₂ + Aryl──Br	$\xrightarrow{1 / [Pd(C_3H_5)Cl]_2}$ $\xrightarrow{H_2O, K_2CO_3, TBAB}$ Aryl				
Entry	Aryl-Br	$T(^{\circ}C)$	Conv. ^b (%)	Yield ^c (%)		
1^d	Br	70	36	24		
2^d		90	98	70		
3		70	98	65		
4	o Br	70	99	81		
5	FBr	70	99	86		
6	O-Br	90	99	75		
7	——————Br	90	78	66		
8	Br	90	95	95		
9	Br	90	15	13 ^e		
10^{f}	X	90	30	2.2^{e}		
10		100	40	35^e		
	Br					
12		90	99	80		
13	MBr	90	33	27		
14^f		90	76	67		
15		100	60	55		
16	⟨Br	90	2	_		
17 ^g		90	21	14		
18	N N N	90	25	20		
19^{f}		90	98	80		
20		100	61	40		
21	S Br	90	98	87		
22	sBr	100	8	_		

^{*a*} Under aerobic conditions: Pd/substrate = 1 : 10 000; aryl bromide: 2.0 mmol; phenylboronic acid: 2.4 mmol; K_2CO_3 : 3.0 mmol; TBAB: 3.0 mmol; 10 mL of H₂O; reaction time: 2 h. ^{*b*} By GLC using *n*-undecane as internal standard. ^{*c*} Isolated yield. ^{*d*} Pd/substrate = 1 : 100 000. ^{*e*} GLC yield. ^{*f*} Reaction time: 22 h. ^{*g*} In EtOH-H₂O 1 : 1 (v/v).

the reactions of 4-bromobenzaldehyde or 1-bromo-4-fluoro benzene (two activated substrates, entries 4 and 5) with phenylboronic acid go to almost complete conversion in only two hours at 70 °C, while with electron-rich deactivated aryl bromides such as 4-methoxybromobenzene and 4-methylbromobenzene it is necessary to increase the reaction temperature to 90 °C to obtain almost complete conversion (entries 6 and 7). Also the moderately sterically demanding 2-methylbromobenzene (entry 8) was efficiently coupled with phenylboronic acid, and only when the substrate is the highly deactivated and hindered 2,4,6-trimethylbromobenzene the reaction rate undergoes a significant decrease (entry 9). Nevertheless, the product yield can be increased either increasing the reaction time (entry 10) or the temperature at 100 °C, at this latter temperature a reasonably good 40% substrate conversion is obtained by only 2 hours (entry 11). Excellent results were obtained also with 1-bromonaphtalene (entry 12).

To further explore scope and limitations of the catalyst, we carried out experiments with some heteroaryl bromides. As expected, significantly lower reaction rates are observed with heteroaromatics substrates. In fact, the reaction of 3-bromopyridine with phenylboronic acid at 90 °C proceeds to only 33% conversion by 2 hours (entry 13). Nevertheless, good conversions can be obtained either by increasing the reaction time or the temperature (entries 14 and 15). The catalytic system showed to be by far less efficient with 2-bromopyridine; in fact, only traces of the coupling product were obtained under the optimized conditions (entry 16). The difference in reactivity between 3- and 2-bromopyridine may be ascribed to the differences in the capability of the two substrates to approach the metal centre.8 Likely, coordination of the more basic 3-bromopyridine9 to the metal centre is favoured when compared to the less basic 2-bromo derivative.¹⁰ According to examples in literature,^{11a,b} often the coupling of halopyridines with phenylboronic acid is successful when carried out employing alcoholswater mixtures as the reaction solvent. This approach revealed to be beneficial since in an experiment carried out under the same conditions of entry 16, but using an EtOH-H₂O mixture (1:1, v/v) as the solvent, we obtained a substrate conversion of 21% by 2 hours. Albeit modest, this conversion arises from a reasonably good reaction rate of about 1000 catalytic cycles per hour. The coupling of 5-bromopyrimidine with phenylboronic acid is efficiently promoted by the catalytic system. Although the substrate conversion is only 25% by 2 hours when the reaction is carried out in water at 90 °C (entry 18), almost complete conversion can be obtained extending the reaction time at 22 hours (entry 19); it is worth to note that a significant increase in the reaction rate can be obtained by setting the reaction temperature to 100 °C (entry 20).

At 90 °C, the reaction of 2-bromothiophene with phenylboronic acid proceeds smoothly affording the desired coupling product in almost complete yield by only 2 hours (entry 21 of Table 3). On the contrary, the catalyst is unable to activate 3bromothiophene, which reaction with phenylboronic acid affords only small amounts of the sought coupling product even when the reaction temperature is increased to 100 °C (entry 22). In contrast to that observed with 2-bromopyridine no improvement was achieved by running the coupling of 3-bromothiophene in water–ethanol mixtures (experiment not reported in Table 3).

Finally, the catalyst efficiency was tested in the coupling of some aryl chlorides. The reactions were carried out employing a substrate to catalyst ratio of 10 000 : 1 and a TBAB/substrate molar ratio of 1 : 1; the temperature was set to 100 °C and the reaction time was of 2 hours. Good results (90% conversion) were obtained only with the activated 4-chloroacetophenone, while with non-activated (chlorobenzene) or deactivated substrates (*e.g.* 4-chloroanisole and 4-chlorotoluene) only modest conversions in the 5–10% range were achieved. No substantial improvement in product yield was obtained by increasing the reaction time suggesting that the catalyst has a limited longevity when employed with aryl chlorides. Experiments carried out at higher catalyst loadings afforded no better yields and resulted in extensive precipitation of palladium black.

Summing up, the catalytic activity of our system appears comparable to that of other catalysts¹¹⁻¹⁵ able to efficiently promote the coupling of aryl bromides but displaying inadequate activities with aryl chlorides. It is to emphasize that our catalyst, based on a simply designed ligand, shows an important longevity so that the reaction can be carried out employing as little as 0.001–0.01 mol% of palladium. This feature combines favourably with catalyst reusability, and the positive impact on the economical and practical aspects of the catalytic process is obvious. In this connection, it is worth to note that there is a limited number of catalysts able to activate aryl chlorides in water.¹⁶

Experimental

Preparation of sodium 2-(1-((pyridin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)ethyl sulfate (1)

To a suspension of but-3-ynyl sodium sulfate¹⁷ (455 mg, 2.6 mmol) in a mixture of *t*-BuOH (15 mL) and H₂O (1 mL) were added a solution of 2-(azidomethyl)pyridine (3.57 mg, 2.7 mmol) in *t*-BuOH (5 mL), and, finally, a solution of $Cu(OAc)_2 \cdot H_2O$ (26 mg, 0.13 mmol) in water (0.5 mL). The mixture was stirred under inert atmosphere for 48 hours, then the liquid phase was taken to dryness to give a green solid. Flash-chromatography (silica gel, tetrahydrofuran-methanol 6 : 4) affords the title compound as a white solid which was dissolved in methanol and precipitated with diethylether (525 mg, 66%).

Preparation of the catalyst stock solutions

 10^{-2} M catalyst stock solutions were prepared by diluting with water in a 10 mL volumetric flask a methanol solution (3 mL) containing 19.5 mg (0.05 mmol) of $[Pd(\eta^3-C_3H_5)Cl]_2$ (ref. 18) and 30.8 mg (0.1 mmol) of **1**.

Typical procedure for the cross-coupling reactions

All manipulations were carried out under aerobic conditions. In a typical experiment (entry 2 of Table 1), 4-bromoacetophenone

(2.0 mmol), phenylboronic acid (2.4 mmol), potassium carbonate (3.0 mmol) and tetrabutylammonium bromide (3.0 mmol) were added into a glass reactor (50 mL of volume) and suspended in 10 mL of water. To the stirred suspension, 100 μ L of the 10^{-2} M catalyst stock solution were added and the mixture was heated to 90 °C. After 2 hours the suspension was rapidly cooled to room temperature and extracted with ethyl acetate (3 × 5 mL). The organic phases were reunited and after addition of *n*-undecane (internal standard) analyzed by GLC.

Conclusions

We have prepared a new water-soluble nitrogen ligand and developed a simple protocol for the Suzuki–Miyaura reaction. The coupling of a variety of aryl bromides and heteroaryl bromides with phenylboronic acid has been successfully carried out in reasonable reaction times using very low catalyst loadings. The catalytic system works under conventional heating, is air stable and can be employed for three successive runs with negligible loss of efficiency.

It is finally worth to note that **1** must be considered the prototype of a new family of water-soluble ligands since both its steric and electronic characteristics can be easily tuned taking advantage of the modular nature of the copper-catalyzed [3 + 2] Huisgen cycloaddition.

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