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Review

Pd–benzothiazol-2-ylidene complex in ionic liquids: Efficient catalyst for carbon–carbon coupling reactions

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Dedicated to Professor Giorgio Modena on the occasion of his 80th birthday.

Abstract

Pd-benzothiazol-2-ylidene complex **3** catalyzes efficiently the carbon–carbon coupling reactions in the ionic liquid tetrabutylammonium bromide (TBAB) as solvent. The IL does exert a striking influence on the reactivity and the stability of the catalyst. This is probably due to the formation, by reaction with TBAB, of an anionic and more nucleophilic complex surrounded by large tetrabutylammonium cation that would impede, by imposing a Coulombic barrier for collision, the formation of clusters growing further into catalytically inactive metal particles. On the contrary, ionic liquids with planar structures and poor nucleophilic anions like the [bmims], that form tight ion pairs, are barely efficient in influencing the reactivity and stability of the catalyst.

Keywords: Benzothiazole carbenes ligands; Catalysis; Ionic liquids; Palladium; C–C coupling

Contents

1. Introduction

Nucleophilic *N*-heterocyclic carbenes, the imidazol-2-ylidene, ever since the early reports by Öfele [1] and Wanz-

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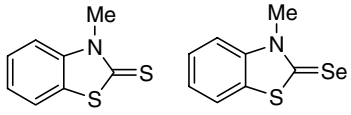
lick [2] have attracted growing interest as possible alternative for phosphines ligands in homogenous catalysis [3]. Herrmann and co-workers [4] reported the application of a palladium complex with imidazol-2-ylidene as ligands to the Heck reaction. Contrary to the imidazol-2-ylidene carbenes [5], the isolation of thiazolium and benzothiazolium-derived free carbenes, though the great deal of efforts in studying the thiazolium chloride (vitamin B1) [6], was unsuccessful [7,8], due to their fast dimerization and instability [9–12]. The synthesis of a palladium complex with benzothiazole carbene and a phosphine as ligands was reported by Lappert [13] with no application for synthetic purposes.

2. Results and discussion

Some years ago [14,15], we succeeded in trapping benzothiazole carbene by reaction, in pyridine, of 3-methylbenzothiazolium iodide with sulfur and selenium to give **1** and **2**, respectively.



1 **2**

Compound **1** allowed the conversion of epoxides into episulfides and **2** did deoxygenate stereospecifically epoxides into olefins.

Owing to the good results obtained by the Herrmann's Pd-imidazol-2-ylidene [4] catalyst in the Heck reaction, we synthesized the palladium catalyst **3** by reaction, in THF, of 3-methylbenzothiazolium iodide with palladium acetate (Fig. 1) which proved to be stable to air, moisture and high temperatures [16].

The complex **3** did catalyze efficiently, in DMF and DMA, the Heck [17] reaction of activated aryl bromides and iodobenzene with very high TONs values (Turnover Number), the latter up to a million, but was inefficient for reactions of the less reactive bromo and chloro aromatics (Scheme 1).

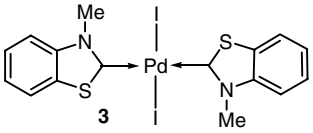


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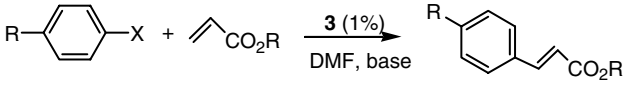
Fig. 1. Structure of catalyst **3**.



R= H or EWG;X= I, Br

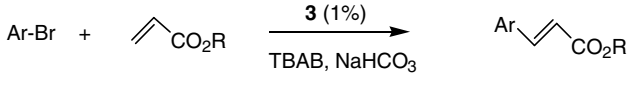
Scheme 1.

Among the various solvents utilized in the Heck reaction, in the last 10 years, the imidazolium-based ionic liquids (ILs) have been utilized [18] as "green solvents". However, under these reaction conditions, only the aryl iodides react with high conversions, whereas the aryl bromides, are partially reactive or require high temperatures and catalyst concentrations [19]. For this reason, to activate the aryl bromides in these ILs, the addition of phosphines as ligands is indispensable [20]. As the previous reports [4,21–23] on the Heck reaction recognized that the addition of tetraalkylammonium or tetraphenylphosphonium salts to conventional solvents led to higher catalytic activity, we decided to perform this reaction in tetrabutylammonium bromide (TBAB) as solvent [24]. The complex **3** proved to be an excellent catalyst in the phosphine-free Heck reaction of the aryl bromides and activated aryl chlorides in TBAB (Scheme 2) [25].

The coupling reactions were very fast (less than 3 h) in comparison with conventional procedures and occurred in high yields in the presence of a cheap and eco-friendly base such as sodium bicarbonate in high yields. In addition, this procedure allowed an easy separation of the reaction products either by vacuum distillation or extraction with solvents immiscible with TBAB thus leaving both the IL and the catalyst that can be further recycled.

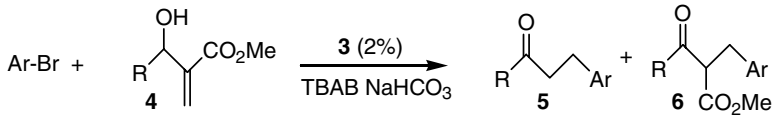
In most of the papers dedicated to the Heck reaction, no more than few examples have been reported dealing with methacrylates as olefin acceptors [23,26]. Among these, it was reported [27] that the arylation of 3-hydroxy-2-methylenealkanoates affords β-oxoalkanoates (Scheme 3). Beside the harsh reaction conditions necessary for the reaction of α-substituted acrylates, the arylation of 3-hydroxy-2-methylenealkanoate suffers also from a competitive retro-Baylis–Hillman reaction and further arylation of the β-oxoalkanoate end product [28–30]. On the contrary, the catalyst **3** was stable in TBAB melt and efficiently allowed the reaction of various *p*-substituted bromoaromatics with hydroxymethylenealkanoates **4** to give β-arylketones **5** without the expected product, β-oxoalkanoates [27] **6** (Scheme 3). This reaction is synthetically important for the synthesis of non-steroidal anti-inflammatory drugs like the Nabumetone.

The reaction of electron-rich and electron-poor aryl bromides afforded β-aryl ketones in the presence of **3** (2%), sodium formate as reducing agent for palladium and sodium bicarbonate as base [31].



Ar= Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, 2-Naphthyl, 6-MeO-2-Naphthyl

Scheme 2.



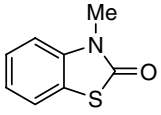
Ar= *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$MeCOC_6H_4$, 2-Naphtyl. R= Ph, Me, *i*-propyl, *n*-propyl, *n*-octyl

Scheme 3.

As some β,β-diaryl acrylates are useful intermediates for the synthesis of the angiotensin II antagonist [32], the platelet activating factors antagonist [33], and the SRS-A antagonists (slow-reacting substance of anaphylaxis) [34], the development of an efficient process for the Heck arylation of β-substituted acrylates would be of significant utility. Usually, the arylation of β-substituted, α,β-unsaturated enoates requires harsh reaction conditions, cyclopalladated phosphanes [26,35] or palladium acetate as catalysts, sterically hindered tertiary amines as bases and quaternary ammonium salts as phase-transfer agents in DMF or DMA as solvents [23]. On the contrary, the catalyst **3** efficiently allowed the reaction of various *p*-substituted bromoaromatics and *p*-chloronitrobenzene with (*E*)-ethyl cinnamate in TBAB melt as solvent [36] (Scheme 4).

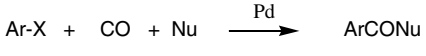
It was also possible to obtain, under the same reaction conditions, an one step synthesis of β,β-diaryl acrylates by reaction of ethyl acrylate with two equivalents of the same aryl bromide.

In every case, however, the coupling process was devoid of stereoselectivity. This finding is of considerable interest since the generally accepted mechanism for the Heck arylation of disubstituted alkenes predicts that the trisubstituted alkene should be formed in a stereospecific manner. The observed lack of stereoselectivity is probably due, as proposed by Buchwald et al. [23] to the equilibration of β,β-diaryl acrylates following the Heck arylation. Therefore, the stereochemistry of these reactions would be defined by base-catalyzed isomerization of products leading to the accumulation of the more thermodynamically favourite isomer. This hypotesis was verified by dissolving either the stereoisomer **7** or **8** in TBAB in the presence of sodium bicarbonate under the same reaction conditions utilized for the coupling process. After prolonged reaction times, however, no isomerization was observed. Any isomerization again was observed by using different organic or inorganic bases [37]. The replacement of TBAB with [bmim] Br as solvent, decreased significantly the reaction rate without an increase of the stereospecificity. Another rationalization implies the re-addition of PdH to the reaction products, followed by isomerization, if the hydride is not neutralized fast by a base. This latter process is well-known as it leads to the isomerization of alkenes, which results in the formation of isomeric Heck products with wrong stereochemistry [38–40]. The replacement of sodium bicarbonate with tetrabutylammonium acetate (TBAA) as base led to an impressive increase in both stereospecificity and reaction rate with the formation of a single stereoisomer [37]. However, this procedure decomposes the catalyst **3** to give 2-oxo-3-methylbenzothiazole **9** with the formation of Pd nanocolloids that catalyze the reaction [41,42]. The TBAA effect on the stability of **3** was verified by adding an excess of TBAA to **3** dissolved in TBAB at 130 °C. Beside the formation of a black suspension, we did isolate 2-oxo-3-methylbenzothiazole **9** arising from the deligation of the benzothiazol-2-ylidene ligands in **3** (see Section 3). A reaction sample, deposited on carbon film coated TEM grids, revealed the presence of Pd nanoparticles 2–6 nm in size.



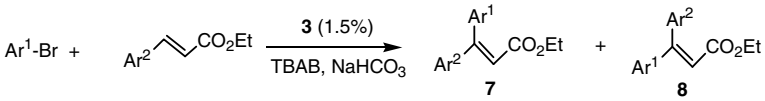
9

The transition-metal catalysed carbonylation of organic halides, in the presence of a nucleophile, is the most common method for the synthesis of aromatic acids and derivatives (Scheme 5) [43]. Among various catalysts, the Pd–phosphine complexes have been widely employed mostly under homogeneous conditions [44].



X= Cl, Br, I; Nu= OH, OR, NR_2

Scheme 5.



Ar^1= *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$MeCOC_6H_4$, 2-Naphthyl, *p*-CN; Ar^2= Ph.

Scheme 4.

However, as a result of the notorious phosphine degradation by P–C bond cleavage, an excess of phosphine is often necessary in order to avoid the catalyst deactivation. Furthermore, the carbonylation of less reactive aryl halides requires high reaction temperatures, which decompose the catalyst and impede further applications. Even a more robust catalyst such as Herrmann palladacycle [45] proved to be inactive. The beneficial effect exerted by TBAB in the Heck reaction prompted us to test the catalytic activity of **3** towards the carbonylation directly in TBAB melt and dissimilar ILs [46]. In the former medium iodobenzene and 4-bromoacetophenone reacted with carbon monoxide at 130 °C ($P_{CO} = 1$–8 atm) in the presence of catalytic amounts of **3**, small stoichiometric excess of BuOH as nucleophile and NEt_3 as base. The catalyst was recycled almost seven times without substantial loss of activity. Nevertheless, while under these conditions the iodobenzene and the activated bromoaromatics reacted easily, the less activated bromo and chloro aromatics required the addition of catalytic quantities of triphenylphosphine to obtain good conversions. Interestingly, the structures of both the cation and the anion influenced decidedly the catalytic activity. Indeed, as shown in Table 1 for the carbonylation of *p*-bromoacetophenone performed in different IL, the quaternary tetrahedral ammonium salt, including Aliquat® 336, were more efficient reaction media than the planar [bmims] and pyridinium salts.

Table 1
Ionic liquid effect on butoxycarbonylation of 4-bromoacetophenone

Ionic liquid	Yields (%)
[bmim$^+$][BF_4^-]	3
[bmim$^+$] [Cl^-]	<1
[bmim$^+$] [Br^-]	16
Bu_4NCl	30
Bu_4NBr	76
Bu_4NI	32
Aliquat® 336	40
N-butylpyridium to sylate	<5

The β-aryl ketones are useful intermediates for the synthesis of medicinal products as **a**–**c** and for this reason the development of efficient synthetic methods would be useful (see Fig. 2).

The Pd-catalyzed arylation of allylic alcohols for the synthesis of β-aryl ketones is poorly regioselective since the reaction leads to a mixture of carbonyl compounds and substituted allylic alcohols (Scheme 6) [47]. Beside this drawback, the choice of aryl halides and bases are restricted to aryl iodides [47a], triflates, [48] diazonium salts and weak bases, since aryl bromides, by requiring more harsh reaction conditions,afford, in the case of primary allylic alcohols, to aldol reaction of the formed aldehydic products.

The catalyst **3**, in TBAB as solvent, was efficient in catalyzing the coupling of aryl bromides and activated chlorides with allylic alcohols at the 3-position affording regioselectively β-aryl ketones or aldehydes and allowing the synthesis of ketones **a**–**c** in high yields [49]. However, the regioselectivity decreased when β-alkyl- or aryl-substituted allylic alcohols were used.

The catalysis of **3**, though very efficient in catalyzing the reactions of aryl bromides and activated chlorides, failed in the coupling of electron-rich aryl chlorides. The activation of low-cost aryl chlorides was achieved by Fu [50] and Choudary [51] by using somewhat expensive hindered phosphines and amines. In the case of the catalyst **3**, the catalytic activity towards the aryl chlorides was ascribed tentatively by us to the nucleophilicity of the metal not sufficiently high to give the oxidative addition. To circumvent this drawback, we synthesized two different benzothiazole catalysts **10** and **11** bearing electron

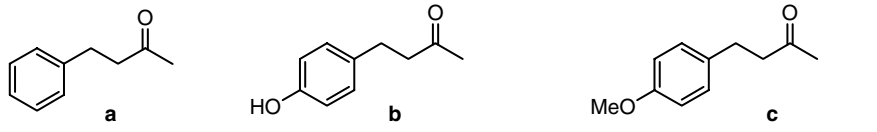
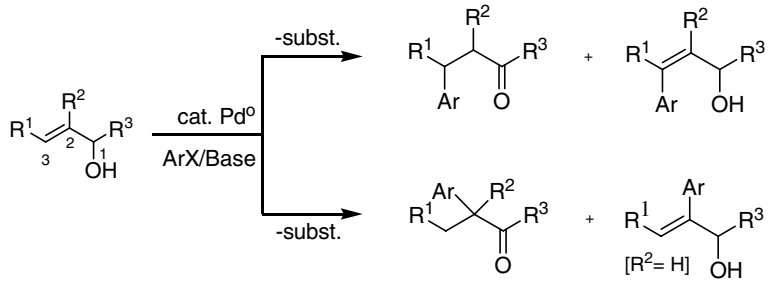
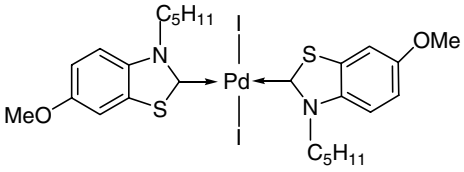


Fig. 2. Biologically active β-aryl ketones synthesized with high regioselectivity by using catalyst **3**.

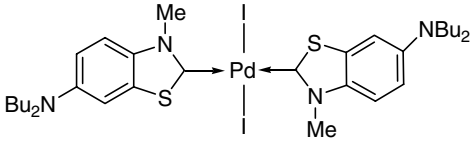


Scheme 6.

releasing groups in the benzene ring whose electronic effect would increase the electron density on palladium and consequently the nucleophilicity of the metal.



10



11

Indeed, both these complexes allowed the coupling of aryl chlorides and in particular **11** up to 80% [52].

As conclusions, two questions arise from all the results reported above: (i) is **3** the true catalyst or a derivative? (ii) why in all the coupling processes the ILs structures do exert a profound effect on the reaction rates and hence on the stability of the catalyst? Surely, the addition of formate or tetrabutylammonium acetate does reduce **3** to Pd nanoparticles as demonstrated by Reetz [53] and us [37] with simultaneous decomposition of the catalyst to give 2-oxo-3-methyl- benzothiazole **9**.

But while by addition of formate to **3** the reactions started immediately, those without the reducing agent occurred with an induction period of about 40 min (Fig. 3) [54].

A similar behaviour was observed by Herrmann [4] on Pd complexes with imidazol-2-ylidene ligands. This probably means that **3** would be transformed into an intermediate and catalytically active specie. To explain the origin of the induction period, we performed the reaction of 2-bromonaphthalene in TBAB with bicarbonate as base and a stoichiometric amount of **3**. Beside the coupling product, we isolated once more **9**, while the catalyst and TBAB were recycled for eight times without the formation of observable ''palladium black''. A probable mechanism for the formation of **9** should consider that TBAB is hygroscopic and that the bicarbonate partially decomposes, under reaction conditions, affording NaOH. These basic conditions can explain the formation of **9** as arising from a nucleophilic substitution of the iodide by hydroxide ion with a probable simultaneous formation of a catalytically active 14-electron catalyst monocarbene palladium(0) complex **12** [55]. The latter could be stabilized by interaction with TBAB to give a dianionic and more stable 16-electron complex $[LPdIBr]^{(2-)}$. This would be not surprising, since in TBAB the bromide ion, being poorly solvated, should be a good nucleophile for palladium. Another possibility is represented by a direct nucleophilic attack of the hydroxide on the heterocyclic nucleus to give the 16-electron complex **13**. (see Scheme 7)

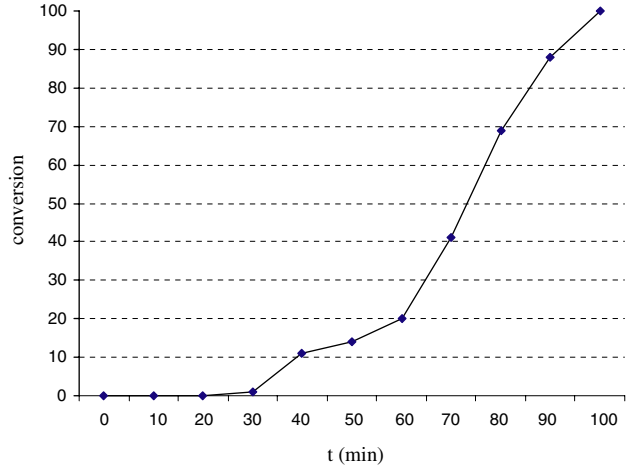
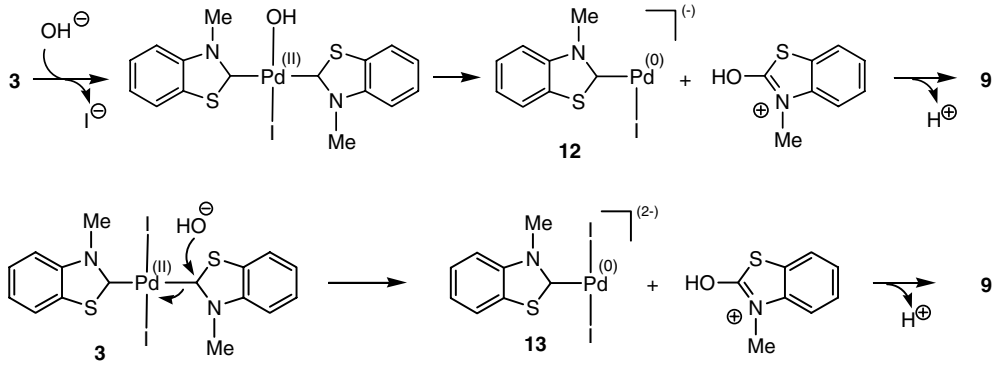


Fig. 3. Induction period for the Heck coupling of bromonaphthalene with butyl acrylate catalyzed by **3** in the absence of reducing agent.

However, this is not the single effect exerted by the TBAB. Indeed, despite the observed beneficial effects due to quaternary ammonium salts on the Heck reaction, the exact nature of this influence cannot be ascribed to a single effect such as the high polarity or phase-transfer ability [56], but rather to an overlap of several factors. For example, Reetz [53,57] and us [37] found that reduction of a Pd salt in THF and in the presence of tetrabutylammonium acetate or formate gave Pd-nanoparticles stabilized by the large ammonium cation. Furthermore, Neghishi et al. [58] and Amatore and Jutand [59] demonstrated that $Pd(0)(PPh_3)_2$, the proposed catalyst in the Heck reaction, was unstable in the absence of halide or acetate ions which transform this complex into a more stable and catalytically active 16-electron anionic complex as $[Pd(PPh_3)_2X]^{(-)}$. The stabilization of the catalytic system by halide salts was also demonstrated by the extension of the lifetime for the Herrmann palladacycle [60]. The stabilizing effect is exerted not only by the bromide ion, which is likely to enter the co-ordination shell of underligated LPd(0) to give the anionic complex, but also by the large tetrabutylammonium cation. Indeed, the formation of a large $[LPdIBr]^{(2-)}[^{(+)}NR_4]_2$ complex, by imposing a Coulombic barrier for collision, should impede the formation



Scheme 7.

of Pd-clusters growing further into metal particles. On the contrary, the ionic liquids bearing different anions such as tosylate or tetrafluoroborate would not stabilize efficiently the 14-electron complex $[LPd(0)I]^-$ like halides can. Evidence for this is provided by the inefficacy of **3** in catalyzing the carbonylation in butylpyridinium tosylate (see Table 1). Furthermore, the ammonium cation could assist electrostatically the polarization or decomplexation of the bromide ion from the Pd(II) complex arising from oxidative addition with aryl bromides and this would render the Pd(II)-complex more electrophilic for a fast olefin insertion. This is conceivable since it was calculated [61], for analogous Pd-complexes with imidazol-2-ylidene carbenes ligands, that the removal of a bromide ion from the oxidative addition complex of aryl bromides is a strongly endothermic process. The control of tetraalkylammonium halides on the catalyst life and efficiency helps to explain the low performances of [bmim] halides as reaction media for the coupling reactions which are due, in our opinion, to the structure of these salts. Indeed, it was demonstrated [62–64] that, contrary to quaternary, tetrahedral ammonium salts, the imidazolium halides have planar structures dominated by strong ion-pairing effects. Therefore, it is plausible that the low availability of halides and cations in stabilizing the catalyst may decrease the catalytic activity [64]. In addition, we found [65] that palladium nanoparticles are not sufficiently stable in imidazolium salts where their rapid aggregation occurred followed by the catalyst deactivation.

3. Conclusions

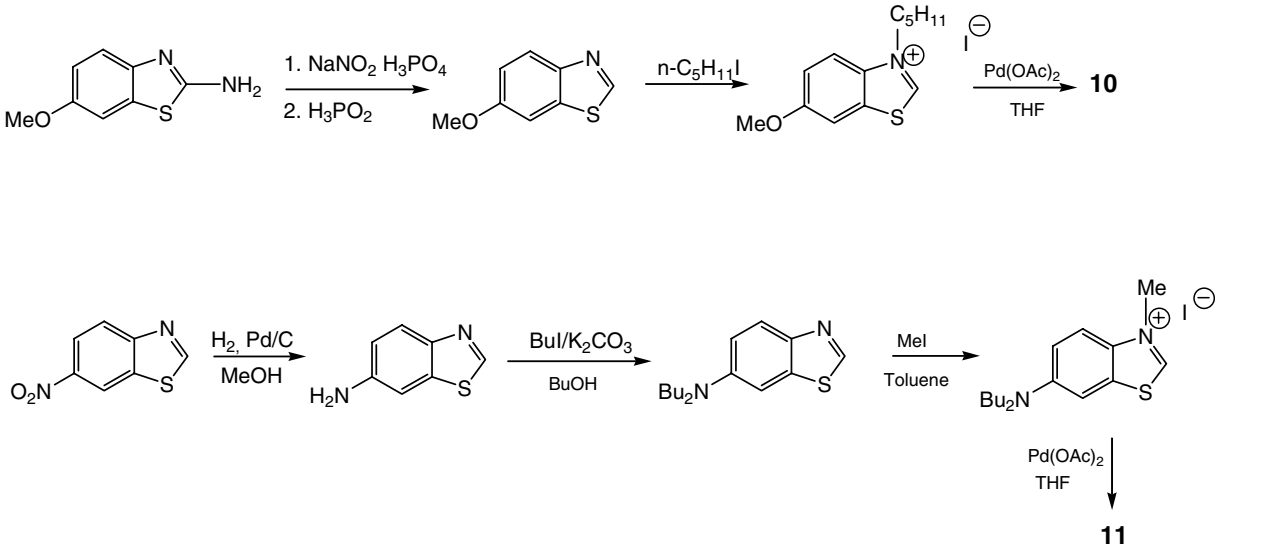
A comparative study on the effects exerted by different ionic liquids on the catalysts stabilization, reaction rates and the regio- and stereo-selectivity in the C–C coupling reactions, reveals the superiority of quaternary ammonium halides towards imidazolium and pyridinium derived ionic liquids. The effects due to the tetrahedral ammonium salts are manifold. The bulkiness of the tetrahedral ammonium ion, by forcing the halides anions away from the cation, renders these more nucleophilic and available for the catalysts activity than the planar $[bmims]^+$ can. Indeed, the planar structures of $[bmims]^+$ and pyridinium cations, by binding tightly the halide ions would decrease their availability. This paper, though the understanding of the mechanism of catalysis in ionic liquids is still in its infancy, because of the lack of surface chemical information about the solvents themselves and solvation of the catalysts, is an effort to contribute in clarifying the effect of IL.

4. Experimental

4.1. General procedures and instruments

^{1}H NMR (500 MHz) spectra were recorded on a Bruker AM 500 MHz and chemical shifts were quoted in parts per million (ppm, δ). GC analyses were carried out on HP 5890A capillary gas chromatograph (ZB-1, 30 m, 0.25 mm i.d.). Elemental analyses were obtained from a Carlo Erba EA1108 microanalyser instrument. All the commercially available chemicals were purchased by Fluka, and solvents used for synthesis of the catalysts **3**, **10** and **11** (toluene and THF) were dried over Na/benzophenone and distilled under nitrogen prior to use. The tetrabutylammonium bromide (Fluka 99%) is hygroscopic by nature and contains traces of tributylamine and tributylamine hydrobromide (each less than 0.5%) and 20 ppm of an iron (III) salt. This IL was used as received because it is very difficult to purify. Different batches of this IL containing slight more or less impurities and moisture do not influence the extent of the induction period in the coupling of bromonaphtalene with the acrylate.

Complexes **10** and **11** were synthesized starting from the commercially available 2-amino-6-methoxybenzothiazole and 6-nitrobenzothiazole, respectively, according to the following scheme:



*4.2. Synthesis of bis (2,3-dihydro-3-pentyl-6-methoxybenzothiazole-2-ylidene) palladium(II) diiodide (**10**)*

1.7 g (10 mmol) of 6-methoxybenzothiazole, prepared by deamination of 2-amino-6-methoxybenzothiazole, were dissolved in 6.2 g (31 mmol) of 1-iodopentane and the mixture was refluxed overnight. After filtration, the solid was washed with hexane and dried under vacuum to give 3.63 g of 3-pentyl-6-methoxybenzothiazolium iodide as a white solid (m.p. 155 °C, yield 90%). To 9.0 mmol of this salt suspended in 200 ml of dry THF under inert atmosphere were added 4.5 mmol of $Pd(OAc)_2$. The reaction mixture was refluxed for 5 h and then, after cooling, filtered to remove the unreacted salt. After the removal of the solvent, the solid was chromatographed on silica gel (eluent dichloromethane) affording **10** as a yellow solid. Crystallization from pentane/$CHCl_3$ furnished 2.9 g (yield 78%, m.p. >250 °C with decomposition). ^{1}H NMR ($CHCl_3$) δ (ppm): 1.02 (6H, t, $J = 7.0$ Hz), 1.50–1.62 (8H, m), 2.25–2.35 (4H, m), 3.90 (6H, s), 4.92 (4H, t, $J = 8.2$ Hz), 7.05 (2H, dd, $J = 9.1$ and 2.5 Hz), 7.25 (2H, d, $J = 2.5$ Hz), 7.54 (2H, d, $J = 9.1$ Hz). ^{13}C NMR 14.10, 22.36, 27.86, 29.27, 55.69, 55.99, 104.68, 114.27, 115.40, 138.30, 138.74, 157.19, 206.68. Anal. calc. for $C_{26}H_{34}I_2N_2O_2PdS_2$ (830.92): C, 37.58; H, 4.12; I, 30.55; N, 3.37; O, 3.85; Pd, 12.81; S, 7.72. Found: C, 37.12; H, 4.02, N, 3.12%.

*4.3. Synthesis of bis 3-[6-(dibutylamino)-2,3-dihydro-3-methylbenzothiazole-2-ylidene] palladium(II) diiodide (**11**)*

6-(Dibutylamino)benzothiazole. In a Schlenck of 250 ml were dissolved 5 g (27.8 mmol) of 6-nitrobenzothiazole in 40 ml of methanol. Then, 1.47 g of Pd/C (5 mol% of Pd) were added and the flask was charged with a hydrogen atmosphere. The reaction mixture was stirred at 60 °C for 26 h and then, after cooling, was filtered to remove the catalyst. Evaporation of the solvent afforded a dark brown oil which was identified by GC-MS as 6-aminobenzothiazole MS (*m*/*z*) 150 (100), 123 (17), 106 (24), 96 (19), 79 (11), 62 (44), 52 (37), 45 (38).

This crude oil was dissolved in 50 ml of 1-butanol and treated with 9.18 g (66 mmol) of K_2CO_3 and 12.9 g (70 mmol) of 1-iodobutane. The mixture was refluxed overnight until the disappearing of the starting reagent (glc). After filtration and evaporation of the solvent, the crude oil was chromatographed on silica gel (eluent petroleum ether/ethyl acetate 3:1) affording 6.2 g (yield 85%) of 6-(dibutylamino)benzothiazole as an yellow oil, MS (*m*/*z*) 262 (30), 219 (89), 177 (91), 163 (100), 150 (24), 134 (35), 107 (11), 57 (22); ^{1}H NMR ($CHCl_3$) δ (ppm): 0.96 (6H, t, $J = 7.4$ Hz), 1.31–1.42 (4H, m), 1.54–1.65 (4H, m), 3.32 (4H, t, $J = 7.6$ Hz), 6.89 (1H, dd, $J = 9.1$ and 2.5 Hz), 7.04 (1H, d, $J = 2.5$ Hz), 7.89 (1H, d, $J = 9.1$ Hz), 8.60 (1H, s); ^{13}C NMR 13.95, 20.30, 29.30, 51.24, 101.85, 112.74, 123.39, 136.03, 144.32, 146.70, 148.23.

3-Methyl-6-(dibutylamino)benzothiazolium iodide. A 70 ml of toluene solution containing 5.9 g (22 mmol) of 6-(dibutylamino)benzothiazole and 6.4 g (45 mmol) of iodomethane was refluxed for 8 h. The yellow precipitate was collected by filtration, washed with petroleum ether and dried under vacuum (yield 73%, m.p. 193–195 °C). ^{1}H NMR (DMSO) δ (ppm): 0.92 (6H, t, $J = 7.4$ Hz), 1.29–1.40 (4H, m), 1.46–1.58 (4H, m), 3.38 (4H, t, $J = 7.4$ Hz), 4.28 (3H, s), 7.24 (1H, dd, $J = 9.4$ and 2.5 Hz), 7.56 (1H, d, $J = 2.5$ Hz), 7.96 (1H, d, $J = 9.4$ Hz), 10.01 (1H, s).

To a suspension of this salt (4.4 g; 10.9 mmol) in 200 ml of dry THF were added 1.2 g (5.4 mmol) of $Pd(OAc)_2$. The reaction mixture was refluxed for 5 h,

cooled and filtered to remove the unreacted salt. After the removal of the solvent, the residual solid was chromatographed on silica gel (eluent dichloromethane) affording **11** (82% yield) as a yellow solid (m.p. >260 °C dec.) that crystallizes from pentane/$CHCl_3$. ^{1}H NMR ($CHCl_3$) δ (ppm): 0.96 (12H, t, $J = 7.3$ Hz), 1.30–1.42 (8H, m), 1.51–1.60 (8H, m), 3.31 (8H, t, $J = 7.6$ Hz), 4.4 (6H, s), 6.75 (2H, dd, $J = 9.2$ and 2.1 Hz), 6.87 (2H, d, $J = 2.1$ Hz), 7.41 (2H, d, $J = 9.2$ Hz). ^{13}C NMR 13.99, 20.93, 29.16, 42.51, 51.28, 102.73, 111.69, 113.45, 135.70, 138.88, 145.90, 202.66. Anal. calc. for $C_{32}H_{48}I_2N_4PdS_2$ (913,11): C, 42.09; H, 5.30; I, 27.80; N, 6.14; Pd, 11.65; S, 7.02. Found: C, 42.35; H, 5.15, N, 6.01%.

*4.4. Heck coupling of 2-bromonaphtalene with butyl acrylate catalyzed by **3** in tetrabutylammonium bromide as solvent*

A pyrex reaction flask was charged with tetrabutylammonium bromide (3 g) and heated at 130 °C. To the stirred molten salt were added 0.11 mmol of **3**, 17.5 mmol of 2-bromonaphtalene, 30 mmol of sodium bicarbonate and 18 mmol of butyl acrylate. Samples of the reaction mixture were drawn every 10 min and extracted with cyclohexane in which the TBAB and the catalyst are insoluble. At the beginning of the reaction (before 40 min) very low conversion rates were observed in the cyclohexane samples but, after this period, the reaction rate increased. After completion of the reaction, the reaction mixture, after cooling, was extracted with cyclohexane leaving the IL and catalyst which were recycled almost for eight runs, though with decreasing catalytic efficiency, with no, naked eye, observable formation of ''palladium black''. A GC-MS analysis of the extract did provide evidence, beside to the coupling product (E)-butyl 3-(2-naphtyl)-propenoate (88% isolated yield), for the presence of **9** and small quantities of tributylamine (less than 2% of the initial concentration of the IL) deriving from the Hofmann elimination of the tetrabutylammonium salt.

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