

Pd–benzothiazole carbene catalysed carbonylation of aryl halides in ionic liquids

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Abstract

The carbonylations of aryl halides with the Pd–carbene catalyst **1** were studied both in molecular solvents and in ionic liquids (ILs). Among the ILs, tetrabutylammonium bromide (TBAB) was found to give better results. Under these conditions the catalyst, when recovered and reused, did not show a significant decrease of activity. The role of TBAB on the catalyst stability is discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbonylation; Aryl halides; Ionic liquids; Palladium–carbene complexes

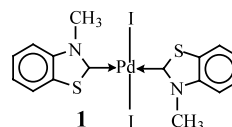
1. Introduction

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 1) [1]. Among various catalysts, the Pd–phosphane complexes have been widely employed mostly under homogeneous conditions [2,3].

However, as a result of the notorious phosphane degradation by P–C bond cleavage [4,5], an excess of phosphane is often required in order to avoid the catalyst deactivation. Furthermore, the carbonylation of less reactive aryl halides often requires high reaction temperatures, which decompose the catalyst and impede further applications. Even more robust catalysts such as Hermann’s palladacycle [6] proved to be inactive.

In the context of our effort to develop efficient and stable catalysts for the Heck reaction [7], we synthesised the Pd–catalyst **1** with benzothiazole carbenes as ligands; they are stable to high temperatures, oxygen and moisture, which catalyses the C–C coupling reactions

both in conventional solvents as dimethylformamide (DMF) or dimethylacetamide (DMA) and in ionic liquids (IL) as tetrabutylammonium bromide (TBAB) [8–10].

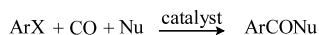


In the latter case, besides very high conversion rates, the catalyst was efficiently recycled several times without metallic palladium deposition. Pd–phosphane catalysts have also been employed for carbonylation processes in IL [11,12], but no example has been reported on the use of Pd–carbene complexes.

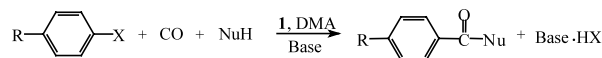
This paper reports some results of our studies on the carbonylation of aryl halides catalysed by **1** and the role exerted by IL on the catalyst activity and stability.

2. Results and discussion

Initially, we tested the efficacy of **1** as a catalyst in DMA (Scheme 2). Iodobenzene and activated aryl bro-



Scheme 1. X = Cl, Br, I; Nu = OH, OR, NR₂.



Scheme 2.

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Table 1
Carbonylation of aryl halides in DMA catalysed by complex **1**^a

Run	Substrate	Base	Cat (%)	Nucleophile	T (°C)	Time (h)	Conv. (%)	Product (yield%) ^b
1	Iodobenzene	Et ₃ N	1	MeOH	80	2	100	C ₆ H ₅ CO ₂ Me (>99)
2	Iodobenzene	AcONa ^c	1	H ₂ O	90	7	100	C ₆ H ₅ CO ₂ H (>99)
3	Iodobenzene	NaOH ^d	1	OH [−]	100	5	95	C ₆ H ₅ CO ₂ H (90)
4	<i>p</i> -Bromoacetophenone	AcONa ^c	2	H ₂ O	130	10	100	4-CH ₃ COC ₆ H ₄ CO ₂ H (95)
5	<i>p</i> -Bromoacetophenone	Et ₃ N	2	MeOH	130	5	95	4-CH ₃ COC ₆ H ₄ CO ₂ Me (91)
6	<i>p</i> -Bromoacetophenone	Et ₃ N	2	Et ₂ NH	130	6	95	4-CH ₃ COC ₆ H ₄ CONEt ₂ (95)
7	Bromobenzene	Et ₃ N	2	MeOH	150	14	>1	C ₆ H ₅ CO ₂ Me (traces)
8 ^e	Bromobenzene	Et ₃ N	2	MeOH	130	14	40	C ₆ H ₅ CO ₂ Me (35)
9 ^f	Bromobenzene	Et ₃ N	2	MeOH	130	14	89	C ₆ H ₅ CO ₂ Me (85)

^a In all experiments, DMA (6 ml), haloarene (4 mmol), MeOH (2 ml), Et₃N (2 ml) and catalyst **1** (1–2 mol%).

^b GLC yields evaluated by using diethylene glycol di *n*-butyl ether as internal standard.

^c AcONa·3H₂O (12 mmol) was used.

^d NaOH (12 mmol) was used.

^e PPh₃ (4 mol%) was added.

^f PPh₃ (4 mol%) and TBAB (1 g) were added.

Table 2
Carbonylation of less reactive aryl halides in DMA catalysed by **1** in the presence of TBAB/PPh₃ at atmospheric pressure of CO^a

Run	X	R	NuH	T (°C)	Time (h)	Products (yield) ^b
1 ^c	Br	H	H ₂ O	130	7	C ₆ H ₅ CO ₂ H (95)
2	Br	H	MeOH	130	4	C ₆ H ₅ CO ₂ Me (95)
3	Br	H	Et ₂ NH	130	5	C ₆ H ₅ CONEt ₂ (85) ^d
4 ^c	Br	CH ₃	H ₂ O	130	12	<i>p</i> -CH ₃ C ₆ H ₄ CO ₂ H (87)
5	Br	CH ₃	MeOH	130	5	<i>p</i> -CH ₃ C ₆ H ₄ CO ₂ Me (>99)
6	Br	CH ₃	Et ₂ NH	130	7	<i>p</i> -CH ₃ C ₆ H ₄ CONEt ₂ (91)
7 ^c	Br	OCH ₃	H ₂ O	130	7	<i>p</i> -CH ₃ OC ₆ H ₄ CO ₂ H (85)
8	Br	OCH ₃	MeOH	130	7	<i>p</i> -CH ₃ OC ₆ H ₄ CO ₂ Me (95)
9	Br	OCH ₃	Et ₂ NH	130	7	<i>p</i> -CH ₃ OC ₆ H ₄ CONEt ₂ (93)
10 ^c	1-Br-naphthalene		H ₂ O	130	7	1-NaphthylCO ₂ H (55)
11	1-Br-naphthalene		MeOH	130	7	1-NaphthylCO ₂ Me (66)
12	1-Br-naphthalene		Et ₂ NH	130	7	1-NaphthylCO ₂ NEt ₂ (90) ^d
13 ^c	Cl	CH ₃ CO	H ₂ O	140	10	<i>p</i> -CH ₃ COC ₆ H ₄ CO ₂ H (45)
14	Cl	CH ₃ CO	MeOH	140	10	<i>p</i> -CH ₃ COC ₆ H ₄ CO ₂ Me (53)
15	Cl	CH ₃ CO	Et ₂ NH	140	10	<i>p</i> -CH ₃ COC ₆ H ₄ CONEt ₂ (17)
16 ^c	Cl	NO ₂	H ₂ O	140	9	<i>p</i> -CH ₃ COC ₆ H ₄ CO ₂ H (30)
17	Cl	NO ₂	MeOH	140	10	<i>p</i> -CH ₃ COC ₆ H ₄ CO ₂ Me (15)
18	Cl	NO ₂	Et ₂ NH	140	10	<i>p</i> -CH ₃ COC ₆ H ₄ CONEt ₂ (39)

^a In all experiments, DMA (6 ml), haloarene (4 mmol), MeOH or Et₂NH (2 ml), Et₃N (2 ml), TBAB (1g), PPh₃ (8 mol%) and catalyst **1** (4 mol%) were used.

^b GLC yields.

^c AcONa·3H₂O (12 mmol) was used.

^d Isolated product.

mides were carbonylated with good yields at atmospheric pressure of CO and under relatively mild temperature conditions (Table 1, runs 1–6), but less reactive aryl halides such as bromobenzene, required the addition of triphenylphosphane and TBAB to give in good yields the methoxycarbonylation (runs 7–9).

These reaction conditions were also extended to the carbonylation of other less reactive substrates in the presence of various nucleophiles. In all cases, to obtain high conversions, it was necessary to add both phosphane and TBAB (Table 2).

The beneficial effect exerted by TBAB prompted us to test the catalytic activity of **1** towards the butoxycarbonylation directly in TBAB melt and other ILs. This is important since most of the traditional solvents used in organic synthesis have been found “damaging to the environment”, so the utilisation of ILs can contribute to decrease the environmental contamination by toxic and volatile solvents.

Thus, iodobenzene or 4-bromoacetophenone were allowed to react with a carbon monoxide pressure ($P_{\text{CO}} = 1\text{--}8$ atm) into TBAB melt, in the presence of

Table 3

Butoxycarbonylation of aryl halides in TBAB melt ^a

Run	Aryl halide	Catalyst	<i>T</i> (°C)	<i>P</i> _{CO} (atm)	Conv. (%)	Butyl ester yield (%) ^b
1	Iodobenzene	1	100	1	89	85
2	4-Bromoacetophenone	1	130	1	10	3
3	4-Bromoacetophenone	1	130	4	25	22
4	4-Bromoacetophenone	1	130	8	78	76
5	4-Bromoacetophenone	Pd(OAc) ₂ /PPh ₃ ^c	130	8	95	78
6	Bromobenzene	1	130	8	30	27
7	Bromobenzene	1/PPh ₃ ^c	130	8	96	85

^a In all experiments a 5:1 ca. molar ratio TBAB–aryl halide has been used, which produces, at reaction temperature, a quite fluid melt to be easily stirred: TBAB (6 g, 18.6 mmol), ArX (4 mmol), BuOH (4.8 mmol), Et₃N (5.2 mmol), catalyst (1 mol% of Pd); reaction time 14 h.

^b GLC yields evaluated by using diethylene glycol di *n*-butyl ether as internal standard.

^c PPh₃ (3 mol%) was used.

catalytic amount of **1**, small stoichiometric excess of BuOH, as nucleophile, and NEt₃ as base.

The results in Table 3 show that only iodobenzene was carbonylated at atmospheric pressure, while for other substrates higher pressures are needed (Table 3, runs 1–4) and the butoxyester yields rise when the CO pressure increases. This behaviour could be accounted for by an increasing of CO solubility into the IL as well as for a faster insertion of CO into the palladium–carbon bond of the generally accepted aryl intermediate complex. It is well known [2b] that aryl halides carbonylation is initiated by a Pd(0) species which forms an aryl–Pd–X intermediate followed by coordination and CO insertion into the Pd–aryl bond. The nucleophilic attack on the resulting Pd–acyl complex furnishes the carboxylic derivative and regenerates the initial active species (Fig. 1). Also under these reaction conditions, the less reactive aryl halides, such as bromobenzene, required addition of PPh₃ to be carbonylated (Table 3, runs 6–7).

2.1. Catalyst activity and role of TBAB and phosphane

In the literature some scattered data on the influence of ILs on the catalysts performance are reported but no explanation was given. It appears that both the cation and anions of IL play an important role on the catalyst activity and stability. Reetz et al. [13] found that reduction of a Pd salt in THF, in the presence of tetrabutylammonium acetate or formate, gave Pd-nanoparticles stabilised by the large ammonium cation. Furthermore, Neghishi et al. [14] and Amatore and Jutand [15], demonstrated that (PPh₃)₂Pd(0), the proposed catalyst in the Heck reaction, is unstable in the absence of halide or acetate ions which transform this complex in a more stable and catalytically active 16-electron anionic complex as [Pd(PPh₃)₂X]^(–). The stabilisation of catalytic systems by halide salts was also demonstrated by extending the lifetime of the Herrmann palladacycle [6]. We believe that in our system the reduction of **1** leads to an underligated L₂Pd(0), a rather unstable

14-electron complex, which, by reaction with TBAB, affords a stable and catalytically active 16-electron complex [L₂PdBr]^(–)(⁺)NR₄. This would not be surprising since in TBAB the bromide ion, being poorly solvated, would be a good nucleophile for palladium. In this view, ILs having poorly coordinating anions as tosylate or fluoroborate should not stabilise the 14-electron complex L₂Pd(0). Consistent with these observations are our data showing the inefficacy of **1** to catalyse the carbonylation in butylpyridinium tosylate or imidazolium salts (Table 4, entries 1 and 8). This anion effect was also observed [16] in imidazolium tetrafluoroborate. Concerning the activating effect of halides, our data show the following efficacy order: Cl[–] ≈ I[–] < Br[–] (Table 4, entries 4–6). These results could be accounted with a different coordinating power of the anions. Indeed, while the I[–] ion is less coordinating than the Br[–], Cl[–] is too coordinating towards palladium, thus it would make slower the successive CO insertion process.

As far as the influence of the cation is concerned, the formation of a large [L₂PdBr]^(–)(⁺)NR₄ complex, by imposing a Coulombic barrier for collision, should impede the formation of palladium clusters. Furthermore, the ammonium cation could electrostatically assist the polarisation or deligation of the bromide ion

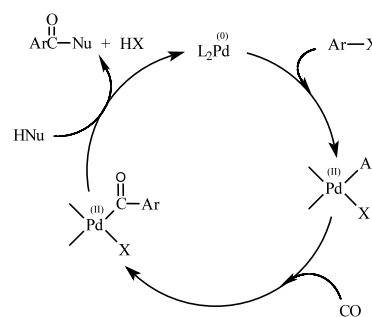


Fig. 1. Generally accepted catalytic cycle for the carbonylation of aryl halides.

Table 4
IL effect on butoxycarbonylation of 4-bromoacetophenone^a

Run	IL	Yield ^b
1	[bmim ⁺] [BF ₄ ⁻] ^c	3
2	[bmim ⁺] [Cl ⁻]	<1
3	[bmim ⁺] [Br ⁻]	16
4	Bu ₄ NCl	30
5	Bu ₄ NBr	76
6	Bu ₄ NI	32
7	Aliquat ^d	40
8	<i>N</i> -Butylpyridinium tosylate	<5

^a In all experiments, 4-bromoacetophenone (4 mmol), catalyst **1** (1 mol%), *T* = 130 °C, reaction time 14 h, *P*_{CO} = 8 atm, IL/substrate ratio 5:1.

^b GLC yields.

^c 1-Butyl-3-methyl imidazolium tetrafluoroborate.

^d Tricaprylmethyl ammonium chloride.

from the anionic Pd(II) pentacoordinated complex [L₂PdArBr₂]⁽⁻⁾NR₄⁽⁺⁾, deriving from the oxidative addition with aryl bromides, and this would render the Pd(II)-complex more electrophilic for a fast CO insertion. This is conceivable since it was calculated, for analogous Pd-complexes with imidazolyl carbenes ligands, that the removal of bromide from the [L₂PdArBr₂]⁽⁻⁾ complex is a strongly endothermic process [17].

Other evidence on the influence of the cation arises from the comparison of the carbonylation efficiency in NBu₄Br and [bmim⁺] [Br⁻] (Table 4, entries 3 and 5). We believe that the better performance of TBAB as solvent could be ascribed to the structural differences between the [NBu₄⁺] and [bmim⁺] cations, which could influence the anion behaviour. Indeed, the bulkiness of the tetrahedral ammonium ion forces the bromide ion away from the cation and this decreased electrostatic interaction would render the bromide ion more available for palladium complex stabilisation or, in other words, more “nucleophilic”. On the contrary, the planar [bmim⁺] cation, by binding the anion tightly, would render this latter less available for palladium.

In an attempt to gain evidence on the formation of the active (benzothiazolylidene)₂Pd(0) species, the Pd^{II}-catalyst **1** was reduced in THF at 50 °C with a slight excess of sodium formate. The resulting red–brown solution was submitted to a stream of CO and its IR spectrum was recorded. No absorption bands ascribed to the stretching of CO were observed. Addition of iodobenzene did not cause the appearance of a band assignable to the CO of the expected acyl complex, but when the reaction temperature was raised to 90 °C, the IR spectrum displayed two weak bands centred at 1770 and 1630 cm⁻¹. These bands could be assigned, respectively, to the ν_{CO} of Pd–COR group and to the ν_{CO} of iodobenzoyl formed by reductive elimination.

Another intriguing point is the role of PPh₃ on the carbonylation of the less reactive halides. A question is whether in these cases the benzothiazole ligand is still bonded to palladium. In order to get some insight we carried out the carbonylation of 4-bromoacetophenone in TBAB using Pd(II)–acetate/PPh₃ as catalyst (Table 3, run 5). In this case we observed the formation of small amounts of metallic palladium, which caused the deactivation of catalyst when it was reused (Fig. 2). On the contrary, only a slight deactivation was observed in the same reaction catalysed by **1** (see below).

This behaviour could be justified by assuming that the addition of PPh₃ does not cause the substitution of all benzothiazole ligands and the formation of a “(PPh₃)₂Pd(0)” intermediate, as would be in the case of the reaction catalysed by Pd–acetate. Thus, these results accounted for an active species containing both the benzothiazolylidene and the phosphane ligands. Recently, a number of two-coordinated palladium(0) bis(carbene) [18] and mixed Pd(0) or Pd(II) carbene–phosphane complexes [18–20], which efficiently catalyse cross coupling reactions of the aryl halides, have been isolated and characterised.

Finally, a last question concerns the recycling of the catalyst. To check it, after reaction the butyl ester was extracted with diethylether and the solid residue, containing the catalyst and TBAB, was reused under the same reaction conditions to carbonylate other substrate (see Section 3 for details). This procedure was repeated several times. After each reaction, which we consider as a cycle, the organic products were analysed for the yields. The trend of yields for the carbonylation of iodobenzene and *p*-bromoacetophenone versus cycles (Fig. 2), shows that the catalytic activity decreases very

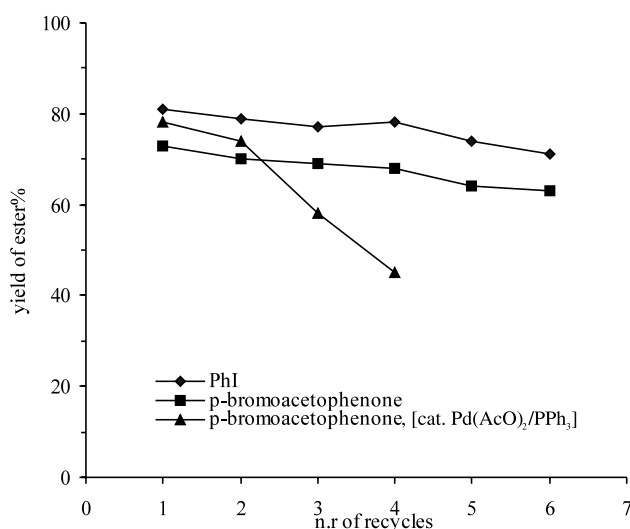


Fig. 2. Recycling of catalytic system TBAB/**1**. Reaction conditions: halide (4 mmol), Et₃N (1.2 equivalents) BuOH (1.3 equivalents), catalyst **1** (1 mol%), *P*_{CO} 1–8 atm. *T* = 100–130 °C (see Table 3). Isolation of products by soxhlet extraction.

slowly. In fact, after each cycle the yields are still very close to the initial value and the observed slight decrease is most likely due to a loss of catalyst during handling and transferring of materials, rather than to its decomposition. Though the by-product triethylammonium halide did not influence the catalyst activity, its increase after each cycle, by rendering more viscous the reaction medium, prevented further reaction after six times.

In conclusion, while some aspects of the catalytic cycle involving Pd–carbene complexes in ILs are not well understood, our results show that ILs cannot be considered only as simple high polarity solvents, but their efficacy is due to several factors which are actually studied by us.

3. Experimental

All chemicals and solvents were purchased from Fluka and used without further purification. The CO gas (purity 99.9%) was purchased from Air Liquide. The catalyst **1** [bis (3-methyl-2,3-dihydro-benzothiazole-2-ylidene) palladium(II) diiodide] was prepared according to our procedure [7]. All the reaction products were identified by means of their mass spectra recorded on a Shimadzu QP5000 instrument. Yields were determined by GLC on a HP 5890A gas-chromatograph by using a capillary column (ZB-1, 30 m, 0.25 mm i.d.) and diethylene glycol di-*n*-dibutyl ether as internal standard. IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer.

3.1. Carbonylation in molecular solvents at atmospheric pressure

In a typical experiment a glass reactor (150 ml) was charged with iodobenzene (4 mmol), NEt₃ (2 ml), CH₃OH (2 ml), catalyst **1** (26 mg, 0.04 mmol) and DMA (6 ml) under N₂ atmosphere. The gas was evacuated and CO was admitted. After reaction (2 h at 80 °C), the mixture was cooled, treated with 60 ml of aqueous HCl (5%) and extracted three times with 30 ml of Et₂O. The combined organic phases were analysed by GLC. The reactions with other substrates and nucleophiles were carried out according to the above procedure. Reaction conditions are given in Table 2.

3.2. Carbonylation under carbon monoxide pressures

In a typical experiment, TBAB (6 g) was placed in a test tube and heated up to melting point (110 °C). Then, 4-bromoacetophenone (4 mmol), catalyst **1** (26 mg, 0.04 mmol), BuOH (4.8 mmol) and triethylamine (5.2 mmol) were added. After cooling the test tube was

placed in a stainless steel autoclave (50 ml) and pressurised with CO (8 atm of CO). The autoclave was heated to the desired temperature (130 °C) and allowed to react with stirring for 14 h. At the end of the reaction, the orange was cooled, the resultant solid was powdered, placed in a Soxhlet apparatus and the organic products were extracted with Et₂O (70 ml). The solid residue containing TBAB, catalyst and Et₃N·HBr was used in another carbonylation process to test the catalyst stability. The reactions with other substrates were carried out according to the above procedure. Reaction conditions are given in Table 3.

Acknowledgements

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