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In Situ Formation of Mixed Phosphine−Imidazolylidene Palladium Complexes in Room-Temperature Ionic Liquids

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Summary: The in situ formation of a mixed phosphine−imidazolylidene palladium complex, ***3****, in the room-temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) has been observed under conditions employed in many palladium-catalyzed coupling reactions. This paper highlights the noninnocent nature of imidazolium-based ionic liquids and the implications of this for ionic liquid mediated palladium catalysis.*

The potential of ionic liquids to replace environmentally damaging solvents across a wide range of chemistries has become an exciting area of current research.[1] This is particularly true in catalysis.[2] Many of the catalytic reactions that have been investigated in ionic liquids have relied upon palladium complexes. Among these have been Heck,[3] Suzuki,[4] Stille,[5] Negishi,[6] and allylic allylation coupling reactions.[7] There has been some speculation that the formation of palladium imidazolylidene complexes may explain the success of many of these reactions.[3c] The catalytic potential of transition-metal imidazolylidene complexes is well-known in a number of reactions, particularly in palladium-catalyzed coupling reactions.[8] Firm evidence for the in situ formation of bis(imidazolylidene)palladium dibromide in 1-butyl-3-methylimidazolium bromide ([bmim]Br) was first reported by Xiao et al. Attempts to replicate these results in other *ambient-temperature* ionic liquids, however, met with no success.[3e]

During our investigations of the optimization of the Suzuki reaction in ionic liquids, we noted that the addition of a source of halide ions prevented the decomposition of the palladium catalyst. An empirical ratio of 4 equiv of halide with respect to the palladium was required. Hence, we chose to investigate this phenomenon. Using Pd(PPh$_3$)$_4$ as the palladium source and NaCl as the halide source in [bmim][BF$_4$] in the presence of bromobenzene or 3-bromopyridine, under conditions similar to those used in the catalytic runs, ESI-MS revealed the presence of [(PPh$_3$)$_2$Pd(bmimy)X]$^+$ (where bmimy = 1-butyl-3-methylimidazolylidene and X = Cl (**3a**), Br (**3b**)), and ^{31}P NMR spectroscopy showed new signals at 22.9 and 21.8 ppm, respectively.[9] The assignments of these spectra were achieved by comparison to ionic liquid solutions of independently prepared samples. The analogous complexes [(PPh$_3$)$_2$Pd(pypyimy)Br]Br (where pypyimy = 1,3-bis(2-pyridyl)imidazolylidene) and the neutral [(PR$_3$)Pd(peimy)I$_2$] (where peimy = 1,3-bis(1′-(*R*)-phenylethylimidazolylidene) and PR$_3$ = PPh$_3$, PCy$_3$) have recently been reported,[10] as have related platinum complexes.[11]

When the reagents were added sequentially, the addition of the aryl bromide to the Pd(PPh$_3$)$_4$/NaCl/[bmim][BF$_4$] mixture initially formed the oxidative addition product **1**, which subsequently afforded a mixture of **3a** and **3b** upon the addition of an aqueous solution of Na$_2$CO$_3$ (Scheme 1; spectral data for the compounds are given in Table 1). When independently prepared samples of **1** were used as the palladium source, **3** was also detected.[12] In the absence of an aryl bromide under otherwise similar conditions, **3a** was

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[9] Into a suspension of Pd(PPh$_3$)$_4$ (0.24 g, 0.21 mmol), NaCl (0.12 g, 2.08 mmol), and aryl bromide (1.25 mmol) in [bmim][BF$_4$] (2.5 mL) was injected a solution of Na$_2$CO$_3$ (0.26 g, 2.5 mmol) in water (1.25 mL). The mixture was heated at 110 °C for 4 h under N$_2$.

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Scheme 1. In Situ Formation of Mixed Phosphine−Imidazolylidene Palladium Complexes

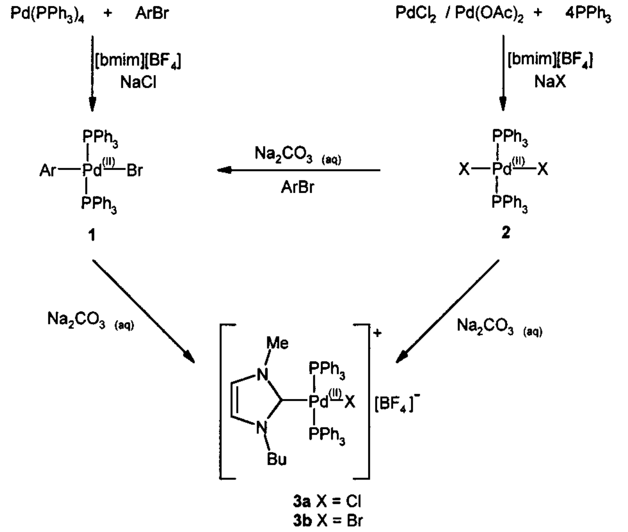

Table 1. Spectral Data for Scheme 1 Compounds Detected in [bmim][BF$_4$]

compd	X	Ar	^{31}P NMR	ESI$^+$ MS
1a		Ph	24.2	707 ([PhPd(PPh$_3$)$_2$]$^+$)
1b		py	24.6	788 ([(Hpy)Pd(PPh$_3$)$_2$Br]$^+$)
2a	Cl		23.9	665 ([Pd(PPh$_3$)$_2$Cl]$^+$)
2b	Br		22.6	709 ([Pd(PPh$_3$)$_2$Br]$^+$)
3a	Cl		22.9	803 ([(PPh$_3$)$_2$Pd(bmimy)Cl]$^+$)
3b	Br		21.8	849 ([(PPh$_3$)$_2$Pd(bmimy)Br]$^+$)

detected only in trace amounts. A mixture of **3a** and **3b** was also detected with the aryl bromide and NaCl using **2** as the source of palladium, either added directly or prepared in situ from Pd(OAc)$_2$ or PdCl$_2$, both with additional PPh$_3$. Employing these sources of palladium in the absence of the aryl bromide afforded only **3a**. Hence, the formation of **3b** in the ionic liquid is the result of the presence of bromide ions originating from the oxidative addition product. Similarly, only **3b** was afforded with NaBr without the aryl bromide.

In a few cases where **3a** was detected without the addition of NaCl, subsequent analysis of the ionic liquid showed that residual chloride from its preparation was still present. After additional washing of the ionic liquid, reactions in these batches of [bmim][BF$_4$] failed to afford **3a** without a chloride additive. Our experience has shown that the preparation of [bmim][BF$_4$] using Na[BF$_4$] rather than [BF$_4$] yields an ionic liquid from which it is easier to remove chloride contamination.

A single-crystal X-ray study of **3a** shows the complex to have crystallographic C_s symmetry about a plane that includes the palladium and chlorine atoms and the imidazolylidene ring system; the *n*-butyl chain is disordered above and below the mirror plane (Figure 1).[13] The imidazolylidene ring is oriented orthogonally to the palladium coordination plane. The geometry at palladium is only very slightly distorted square planar with cis angles ranging between 89.54(7) and 90.54(6)°. The palladium coordination distances are unexceptional. The palladium and its four coordinated atoms are planar to only 0.12 Å, the deviation being a consequence of a distinct nonlinearity in the C−Pd−Cl angle (171.1(4)°); the P−Pd−P angle is essentially linear (178.58(12)°). There are no intermolecular contacts of note.

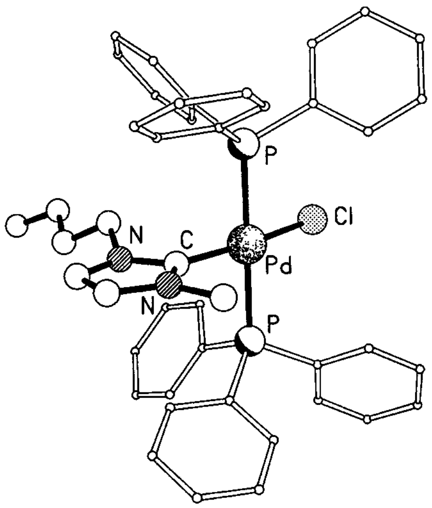

Figure 1. Molecular structure of **3a**. Selected bond lengths (Å): Pd−P = 2.350(2), Pd−Cl = 2.333(4), Pd−C = 1.999(13).

Under our conditions no PdX$_2$(bmimy)$_2$ (where X = Cl, Br) was observed. Attempts to produce these complexes in the absence of PPh$_3$ met with no success. In one case, however, when Pd(OAc)$_2$ was used in the absence of PPh$_3$, with NaBr instead of NaCl, PdBr$_2$(bmimy)$_2$ was observed. We are continuing to investigate why the formation of PdCl$_2$(bmimy)$_2$ is not possible while the formation of **3** can proceed with either Br$^-$ or Cl$^-$.

The in situ formation of **3** from [bmim][BF$_4$] has implications for a number of palladium phosphine catalyzed coupling reactions in [bmim][BF$_4$]. While some reports suggest that the observed enhancements in such reactions can be explained in terms of the unique ionic liquid environment, the involvement of these complexes prepared in situ cannot be discounted. Our preliminary results demonstrate that **3** is extremely active in the Suzuki cross-coupling reaction. Notably, bromobenzene couples with phenylboronic acid, affording biphenyl in a 95% yield (930 TON h^{-1}), with no noticeable catalyst decomposition. Repetitive catalytic runs are also possible without any appreciable loss in activity.

In summary, we have detected the in situ formation of the mixed phosphine−imidazolylidene palladium complex **3** from [bmim][BF$_4$] under conditions similar to many ionic liquid mediated palladium-catalyzed coupling reactions. We have demonstrated that **3** can be prepared from a number of palladium sources, where the halide is directly added or present adventitiously (either from the aryl halide and/or halide contamination of the ionic liquid). Under our conditions we found no evidence for PdX$_2$(bmimy)$_2$. We are continuing to investigate the scope of the catalytic activity of **3** and analogous complexes in a wide range of reactions.

In conclusion, one of the most repeated justifications for the use of imidazolium ionic liquids as solvents for

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(13) Crystal data for **3a**: [C$_{44}$H$_{44}$N$_2$P$_2$ClPd][BF$_4$]·2CHCl$_3$, M_r = 1130.2, orthorhombic, space group *Pnma* (No. 62), a = 18.193(4) Å, b = 23.392(2) Å, c = 11.883(3) Å, V = 5057(2) Å^3, Z = 4 (C_s symmetry), D_c = 1.484 g cm^{-3}, μ(Cu Kα) = 7.37 mm^{-1}, T = 293 K, colorless platelike needles, 3570 independent measured reflections, F^2 refinement, R1 = 0.081, wR2 = 0.211, 2313 independent observed absorptioncorrected reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$), 298 parameters. The high value for R1 is a consequence of disorder in the BF$_4$ counterion and the chloroform solvent molecules. CCDC 167921.

catalysis is that they do not interact strongly with transition-metal solutes. Clearly this is not the case. However, in the case of Suzuki reactions, and possibly in many others, this is actually an advantage.

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Supporting Information Available: Text and tables giving synthetic procedures, full characterization data for compounds **3a** and **3b**, and X-ray crystallographic data for **3**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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