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Accepted Article

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Selective Oxidative Carbonylation of Aniline to Diphenylurea with Ionic Liquids

N. Zahrtmann,[a,b] C. Claver,[a] C. Godard,[a,*] A. Riisager,[b,*] and E.J. García-Suárez[b,c,d]

Abstract: A catalytic system for the selective oxidative carbonylation of aniline to diphenylurea based on Pd complexes in combination with imidazolium ionic liquids is presented. Both oxidants, Pd complexes and ionic liquids affect the activity of the reaction while the choice of oxidant determines the selectivity of the reaction. Together they allow the reaction to proceed under comparatively mild conditions without loss of activity. In-situ NMR examination of the reaction led to the observation of a previously suggested intermediate supporting the proposed mechanism.

Introduction

Ureas are commonly found in the structures of a large number of biologically active compounds. Moreover, ureic derivatives have a wide spectrum of biological activity and have been extensively applied as agrochemicals, dyes, antioxidants or resin precursors as well as key intermediates in organic synthesis, e.g. in the production of isocyanates.[1] In this context, the oxidative carbonylation of amines to obtain ureas (Scheme 1) has received much interest over the past 50 years[2] as alternative to the traditional phosgenation process.[3] The reaction is carried out with a metal catalyst or organo-catalyst, an oxidizing agent such as I₂[1,4] or O₂/air[5] and CO pressure. Among the transition metals and organo-catalysts Mn,[4] Pd,[4c,5h-q,6] Cu,[5a,7] Au,[5b-c] Co,[5d-e] W,[1,4b] Ni,[5f] Rh,[5g] Ru,[5h] S,[8] and Se [9] can be pointed out. Usually, a non-nucleophilic solvent is required in order to avoid the formation of carbamates.[5h,10] The best result reported to date in terms of turn-over-frequency (TOF) was the isolation of tetrasubstituted ureas in I₂-oxidised systems.[6d] The basis of the mechanism suggested by Hiwatari et al. is the observation, that the isolated N-propylcarbamoyl-Pd complex reacts with primary and secondary amines yielding N,N-dialkylurea and N,N,N-trialkylurea, respectively, while the reaction with a tertiary amine forms the free isocyanate (Scheme 2). The selectivity of the reaction supports the mechanism as the reaction step II to III can be promoted by primary, secondary and tertiary amines alike although isocyanate can only be formed from a primary amine and the formation of the urea from isocyanate requires a primary or a secondary amine. The repeated observation that N,N,N,N-tetrasubstituted ureas cannot be generated with CO and secondary amines as the only substrates[9d] supports this mechanism. On the other hand, a different mechanism must be accredited for the observations published first by Pri-Bar et al.[4c] and later by others[9d,9] who prepared N,N,N,N-tetrasubstituted ureas in I₂-oxidised systems. Giannoccaro et al.[4d,5h] prepared Pd-carbamoyl complexes of both primary and secondary aliphatic amines from various Pd(L-L)Cl₂ precursors and isolated the Pd-complexes along with ammonium chlorides supporting the mechanistic proposal by Hiwatari et al.[4d] The Pd-carbamoyl complexes were subsequently treated with C₂H₂, I₂ and CuCl₂ yielding various elimination products along with the Pd²⁺ precursors[4d,5h]. The elimination products were found to be more dependant of the amine substitution than the halide source as secondary

Scheme 1. General reaction scheme for the oxidative carbonylation of amines to ureas.

Scheme 2. Mechanism proposed by Hiwatari and co-workers for the Pd-catalysed oxidative carbonylation of amines.[4d]
carbamoyl halides and primary isocyanates was formed regardless of halide source. Giannoccaro et al.\textsuperscript{[56]} summarized their observations in a proposed mechanism which is largely in agreement with the proposal made by Hiwatari et al.\textsuperscript{[66]} although they disagree on whether or not the ammonium halides reenter the cycle. The formation of secondary carbamoyl halides would explain the observation of N,N,N,N-tetraalkylureas in reactions where I\textsubscript{2} have been used as oxidant as the reaction of carbamoyl halides with nucleophiles is well known.\textsuperscript{[11]} Further support for the proposed mechanisms have been provided by Didigkar et al.\textsuperscript{[59]} and Gabriele et al.\textsuperscript{[5k-5n]} who both studied the oxidative carbonylation of amines with Pd\textsuperscript{2+}/I\textsuperscript{-} catalytic systems using O\textsubscript{2} as oxidant, and reported a correlation between the nucleophilicity and the reactivity of the substrate.

Ionic liquids (ILs) have been employed as reaction media in the oxidative carbonylation of amines generating biphasic systems.\textsuperscript{[5k,5q]} In these reactions, the catalytic systems were constituted by a Pd\textsuperscript{2+} catalysts, an IL - and in the case of Mancuso et al. - an iodide salt as additive.\textsuperscript{[5k]} ILs constitute a special class of compounds that exhibit interesting physical and chemical properties for application in catalysis, biomass processing, electrochemistry etc.\textsuperscript{[12]} In catalysis, ILs can be used as both reaction media and catalysts and provide beneficial effects such as, e.g. high stability towards oxidation by O\textsubscript{2}.\textsuperscript{[12c] In addition, ILs can be easily functionalized for specific catalytic applications.\textsuperscript{[12c-e]}

In this work, we report the use of Pd-based catalysts bearing N- or P-donor ligands for the selective oxidative carbonylation of aniline into diphenylurea in the presence of IL as reaction media. The roles of the IL ions, ligands, oxidants as well as the effect of catalyst loading were investigated and optimized. Introduction of a highly active catalytic system, even under comparatively mild conditions, and observation of the Pd-carbamoyl intermediate previously suggested by Hiwatari and Giannoccaro et al.\textsuperscript{(vide supra) by in-situ NMR spectroscopy, along with a TOF of 15,000 under optimized conditions, are prominent results obtained in the reported study.

Results and Discussion

Influence of oxidant, catalyst loading and reaction time

The influence of the oxidant is important for oxidative carbonylation. O\textsubscript{2} is preferred as a green oxidant but some safety issues have to be considered, i.e. choice of organic solvent due to peroxide formation (e.g. THF or 1,4-dioxane) and concentration of O\textsubscript{2} in the CO/O\textsubscript{2} mixtures to avoid potential explosive hazards.\textsuperscript{[12d]} With this in mind, O\textsubscript{2}, I\textsubscript{2} and 1,4-benzoquinone (BQ) were selected as oxidants in the study. Noteworthy, BQ was used as oxidant for the first time for this reaction type although it has been employed in other well-known Pd-catalyzed processes such as olefins carbonylation.\textsuperscript{[15]} The reaction was initially carried out in a biphasic mixture of toluene and 1-butyl-3-methylimidazolium chloride ([BMIIM][Cl]) at 140 °C under 10 bar of CO using 0.1 mol% of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} as catalyst. The results are displayed in Table 1.

After 4 h of reaction, full conversion aniline was achieved with BQ and I\textsubscript{2} as oxidants while only 79% conversion was obtained with O\textsubscript{2} (Table 1, entries 1-4). The lower conversion in the case of O\textsubscript{2} was attributed to the poor solubility of the gas in the reaction media.\textsuperscript{14} Concerning the selectivity, more than 99% diphenylurea was formed with BQ and O\textsubscript{2} as oxidants (entries 3 and 4). In contrast, no urea product was obtained when I\textsubscript{2} was used without additional additives instead only anilinium chloride formed (entry 1). The absence of urea product with I\textsubscript{2} as oxidant was most likely due to the insolubility of the anilinium chloride species formed from in-situ generated anilinium iodide\textsuperscript{[5h]} and [BMIIM][Cl] during the reaction in the IL phase containing the catalyst, thus hampering the catalytic performance. Similar results were previously reported when I\textsubscript{2} was used as oxidant in the absence of additional base.\textsuperscript{[4c-d,5k]} When the reaction was performed in the presence of K\textsubscript{2}CO\textsubscript{3} (1 equivalent), the conversion decreased to 66% but resulted in >99% selectivity towards urea product (entry 2) as the base scavenge HI which would otherwise be formed in stoichiometric amount with respect to urea.

Table 1. Influence of the oxidant, catalyst loading and reaction time.\textsuperscript{[4c-d]}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Oxidant</th>
<th>Time (h)</th>
<th>TOF\textsuperscript{[b]} (h\textsuperscript{-1})</th>
<th>Conv.\textsuperscript{[c]} (%)</th>
<th>Selec.\textsuperscript{[d]} (%)</th>
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</thead>
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<tr>
<td>1</td>
<td>0.1</td>
<td>I\textsubscript{2}</td>
<td>4</td>
<td>248</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>2\textsuperscript{[a]}</td>
<td>0.1</td>
<td>I\textsubscript{2}</td>
<td>4</td>
<td>165</td>
<td>66</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>O\textsubscript{2}</td>
<td>4</td>
<td>198</td>
<td>79</td>
<td>&gt;99</td>
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<tr>
<td>4</td>
<td>0.1</td>
<td>BQ</td>
<td>4</td>
<td>250</td>
<td>100</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>BQ</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.001</td>
<td>BQ</td>
<td>1</td>
<td>11,000</td>
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<td>BQ</td>
<td>1</td>
<td>7,200</td>
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<tr>
<td>8</td>
<td>0.01</td>
<td>BQ</td>
<td>1</td>
<td>5,200</td>
<td>52</td>
<td>&gt;99</td>
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<td>&gt;99</td>
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<tr>
<td>10</td>
<td>0.01</td>
<td>BQ</td>
<td>0.25</td>
<td>15,600</td>
<td>39</td>
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<td>11</td>
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<td>0.01</td>
<td>BQ</td>
<td>4</td>
<td>1,100</td>
<td>44</td>
<td>&gt;99</td>
</tr>
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</table>

[a] Reaction conditions: Aniline (6 mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, BQ (benzoquinone) (6 mmol), I\textsubscript{2} (6 mmol), O\textsubscript{2} (6 mmol), CO (0.1 mol), 10 bar total pressure, [BMIIM][Cl] (7.5 mmol), mesitylene as internal standard (0.6 mmol), toluene (10.5 mL), 140 °C, 1000 rpm. [b] Turn-over-frequency as mmol aniline converted per mmol Pd per hour. [c] Conversion of aniline. [d] Selectivity to diphenylurea. [e] Using K\textsubscript{2}CO\textsubscript{3} as additive (6 mmol).

Based on the initial results, BQ was selected as oxidant to study the catalyst loading and reaction time effect. When the catalyst loading was progressively decreased from 0.1 to 0.001 mol%, a decrease from full conversion to 11% was observed while the selectivity towards diphenylurea remained unchanged at
>99% (Table 1, entries 6-9). Similarly, the catalyst turn-over-frequency (TOF) increased significantly with the lower catalyst loadings suggesting that only under these conditions was the catalyst inventory utilized efficiently. The influence of the reaction time was also studied at 0.01 mol% catalyst loading (Table 1, entries 8 and 10-12). After 1 h reaction time, a maximum conversion of 52% was achieved whereas longer reaction time resulted in decreased conversions of 47 and 44% after 2 and 4 h, respectively. These results are possibly explained by partly decomposition of the formed diphenylurea into aniline and phenylisocyanate followed by further decomposition into aniline and CO₂ in the presence of water (Scheme 3).\(^{[15]}\) It is worth to point out that the studied catalytic system composed of [BMIM][Cl/Pd-PPh₃/BQ is, to the best of our knowledge, among the most active reported in the literature\(^{[5i-j]}\) with a TOF of 15,600 h⁻¹ after 15 min reaction (Table 1, entry 10).

![Scheme 3. Diphenylurea decomposition to aniline.\(^{[55]}\)](image)

**Influence of the ligand**

Various Pd-complexes with 1,3-bis(2,6-disopropyl-phenyl)-1H-imidazol-3-ium-2-ide (L₁), 1,10-phenantroline (L₂), 3-chloropyridine, aniline (L₃), benzonitrile (L₄) and triphenyl-phosphine (L₅) ligands (Figure 1) were next tested in the oxidative carbonylation of aniline to diphenylurea. The catalytic experiments were performed with a catalyst loading of 0.01 mol% using the corresponding isolated complexes Pd(L₁)₂Cl₂, Pd(L₁)(3-Cl-pyridine)Cl₂, Pd(L₂)Cl₂, Pd(L₃)Cl₂, Pd(L₄)Cl₂, and Pd(L₅)₂Cl₂ synthesized according to previous reports.\(^{[16]}\) The results obtained are displayed in Figure 2.

The highest aniline conversion (52%) was achieved when the Pd(L₅)₂Cl₂ complex was used, whereas slightly lower conversions (47% and 42%) were obtained with the two complexes Pd(L₃)₂Cl₂ and Pd(L₄)₂Cl₂ bearing the monodentate N-donor ligands. The similar results obtained with the latter complexes was probably due to fast replacement of L₄ by L₃ (substrate) resulting in in-situ formation of the same catalytically active Pd-L₃ species. When the PEPPSI complex Pd(L₁)(3-Cl-pyridine)Cl₂ and Pd(L₂)Cl₂ were tested, lower but also similar conversions (26% and 27%, respectively) were obtained. The low conversion obtained with ligand L₂ was somehow unexpected, since very good results were obtained by Shi *et al.* although under more harsh reaction conditions (175 °C and 50 bar CO).\(^{[17]}\) The Pd(L₁)₂Cl₂ complex bearing two NHC ligands showed no activity at all in agreement with previous reports.\(^{[16g-h]}\) Considering the catalytic behavior which have been reported for bis-Pd(NHC)-
complexes an isomerisation from trans- to cis-configuration is required for the addition of the substrate.[18] Given the inflexibility of the applied carbene ligands,[19] this isomerisation is unlikely to take place thus blocking the coordination of the substrate.

In order to elucidate why Pd(PPh3)2Cl2 was the most active pre-catalyst complex, a high pressure (HP) NMR study was performed with this system under in-situ conditions applying 13C{1H}- and 31P{1H}-NMR. At the beginning of the experiment, the 31P{1H}-NMR spectrum (Figure 3, trace 1) displayed one signal at δ = 24.30 ppm in agreement with the characterization of the pure compound.[16b] The addition of aniline caused no change in the spectrum (trace 2), while heating the mixture under Ar lead to a broadening of the signal and an up-field shift to δ = 23.86 ppm (trace 3). No signals belonging to free PPh3 (or O=PPh3) were observed, indicating that the complex was stable under these conditions. Upon the addition of CO gas (trace 4) a signal was immediately observed at δ = -4.70 ppm, assigned to uncoordinated PPh3 in agreement with literature.[72] Heating the reaction mixture under CO to 80 °C (trace 5) lead to a broadening of the signals to an extent where the ligand signal almost disappeared into the background but, in addition, it also resulted in formation of new signal at δ = 24.82 ppm. Heating to 110 °C (trace 6) caused the signals of both free PPh3 and Pd(PPh3)2Cl2 to increase in intensity and width indicating rapid ligand exchange on the metal centre. Furthermore, new signals were observed at δ = 25.16 and 19.79 ppm. Cooling the sample to 25 °C (trace 7) resulted eventually in three distinct signals at δ = 26.64, 24.30 and 19.54 ppm assignable to PdCO2(PPh3)2,[20] PdCl2(PPh3)2Cl2[16b,20a] and PdCl(CONHPh)(PPh3)2[6d] respectively.

Influence of pressure with O2 as oxidant

Initial results using O2 as an oxidant, indicated that low solubility of O2 in the IL caused incomplete conversion of the aniline in the reaction system (Table 1, entry 3). Optimization of the stirring rate was therefore important to maximize gas solubility. Accordingly, the influence of stirring rate was examined for the Pd(PPh3)2Cl2 catalyst system using O2 as oxidant and the results are shown in Table 2 (entries 1-3). Increase in conversion from 41% to 79% was observed when the stirring rate was increased from 500 to 1,000 rpm, but further increase in the stirring rate to 1,400 rpm did not provide any improvement in conversion. This fact confirmed that mass transfer of O2 was rate limiting only with stirring rates below 1000 rpm.
The catalytic performance with varied pressures was also investigated using total pressures of 5-30 bar (Table 3, entries 1-4). An increase in conversion from 55 to 79% was obtained when the total pressure was increased from 5 to 10 bar, whereas further pressure increase to 20 or 30 bar did not improve conversion.

The influence of the amount of IL added in the reaction system was also examined (Table 3, entries 2, 5-7). It was here confirmed, that IL addition improved conversion without affecting the selectivity, and the conversion was quantitative when 30 mmol of the IL was employed. The promoting effect of the IL on the reaction indicated an interaction between the IL and the substrate, the catalyst or the product. The formation of Pd-NHC complexes with Pd-precursors in imidazolium ILs have been reported previously,\cite{5j,16g-h,21} however given the negative effect observed on the reaction when NHC-complexes was applied (Figure 2, entries 1 and 2) in-situ formation of a Pd-NHC complex was not likely to be related to the promoting effect. With respect to possible interactions with the substrate or the product, the unusually high solubility of diphenylurea in [BMIM][Cl] (1:2 molar ratio) lead us to examine the influence of the nature of the IL.

### Influence of ionic liquid with O₂ as oxidant

Physical and chemical properties of ILs are tunable by selecting the appropriate ion combination, which in turn may influence the catalytic performance for a studied reaction. Here, various IL ion compositions were also tested for the oxidative carbonylation of aniline to diphenylurea using the standard reaction conditions shown in Figure 5. 1-Butyl-3-methylimidazolium ([BMIM]+) was selected as the starting cation in combination with different anions, namely iodide, bistriflimide, bromide and chloride.

![Figure 5. Effect of the IL composition. Reaction conditions: Aniline (12 mmol), Pd(PPh₃)₂Cl₂ (0.1 mol%), O₂ (12 mmol), CO (0.1 mol), 10 bar total pressure, IL (15 mmol), toluene (21 ml), mesitylene as internal standard (1.2 mmol), 140 °C, 500 rpm, 1 h. *10 bar (6 mmol O₂).](image)

The best results in terms of conversion were obtained with [BMIM]Br with up to 88% conversion, while [BMIM]Cl provided 76% conversion and [BMIM][(CF₃SO₂)₂N] 57%. Notably, [BMIM]...
inhibited completely the catalytic reaction, which was unexpected since both Gabriele et al.\textsuperscript{[20]} and Peng et al.\textsuperscript{[4]} have described that iodide to play a key role in the catalytic reaction. Didigkar et al.\textsuperscript{[28]} optimized the iodide/Pd-ratio and obtained the highest conversion with 5 eq. of iodide promoter with respect to Pd, whereas both higher and lower ratios resulted in lower conversion. Here, the application of [BMIM]I gave a iodide/Pd-ratio >1,000 suggesting that the high iodide concentration coordinate saturated the catalyst.

The effect of the alkyl substitution on the IL cation was studied comparing results obtained with [BMIM]Cl and [EMIM]Cl (1-butyl-3-methyl-imidazolium chloride), which both yielded identical conversion (76%) (Figure 5). Use of other cations such as [BMIM]\textsuperscript{+} (1-butyl-2,3-dimethylimidazolium) or [TBP]\textsuperscript{+} (tetra-n-butylpyridinium) resulted in no catalytic activity, suggesting that imidazolium cations unsubstituted in the 2-position was required for the reaction. Among the examined anions, bromide gave the best results but ([CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N\textsuperscript{−}] rendered an spontaneous separation of the product and consequently [BMIM][CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N\textsuperscript{−}] was selected for examination of catalyst recyclability. Upon recycling of the catalytic system, a large decrease in conversion was observed from 57% (1st run) to 19% (2nd run) and to 10% (3rd run), clearly showing that the catalyst was not very stable under the applied conditions.

The strong influence of the IL cation could be related to the weak acidity of the C2-hydrogen of imidazolium, which could facilitate increased solubility of the basic aniline substrate.\textsuperscript{[22]} The acidity of imidazolium ILs are known to be affected by the alkyl-substituents and the ion interactions,\textsuperscript{[23]} which should make [BMIM][CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N\textsuperscript{−}] the most acidic of the examined ILs and thus better solvent for aniline.\textsuperscript{[24]} However, the weakly coordinating property of the ([CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N\textsuperscript{−}] anion might have proven insufficient for stabilizing the Pd-species formed during the catalytic cycle. In combination, these opposite effects probably made [BMIM]Br the best compromise between solvation strength and coordination ability. Additional work are ongoing in order to scrutinize the effects of the ILs in more detail.

Conclusions

Selective oxidative carbonylation of aniline to diphenylurea (>99%) was performed with a catalytic system comprised of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} and [BMIM]Cl with a TOF of 15,600 and 1,900 h\textsuperscript{−1} using benzoquinone or O\textsubscript{2} as oxidants, respectively. The catalytic activity achieved with the benzoquinone oxidant is, to the best of our knowledge, the highest reported so far under mildly reaction conditions (140 °C and 10 bar). In addition, HP-NMR experiments provided the first in-situ observation of a proposed Pd-carbamoyl intermediate confirming the trans-conformation of the complex. To investigate the influence of ILs on the reaction, several IL ion compositions were tested and the best results were achieved with [BMIM]Br while the employment of [BMIM][CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N\textsuperscript{−}] facilitated spontaneous product separation. Recycling experiments with the latter IL showed that the resulting catalytic system was reusable in three consecutive reaction runs but with significant loss of activity which was attributed to instability of the catalytically active Pd-species. Work currently undertaken by our group aims to improve the understanding of the role played by the IL and to optimize the catalytic system to improve its durability.

Experimental Section

General

Solvents for synthesis of ILs and Pd-complexes were supplied by Panrec and dried before use with a MBrna MB-SPS-800 solvent purification system or distilled by standard techniques (acetonitrile and ethyl acetate from CaH\textsubscript{2} and THF from Na/benzophenone). ILs were obtained from Sigma-Aldrich or synthesized by literature method and dried under vacuum (70 °C, >24 h) prior to use. Syntheses of ligands and Pd-complexes were performed in flame-dried glassware under argon using Schlenk technique or in a dry nitrogen glove box when necessary. All other chemicals were supplied by Sigma-Aldrich in analytic grade and used as received. NMR analysis was performed on Bruker, Variant or Oxford 400 MHz instruments with deuterated solvents (Oxford Isotopes). \textsuperscript{1}H NMR and \textsuperscript{13}C\textsuperscript{1}H) NMR spectra were referenced to residual solvent peaks as published by Fuller et al.\textsuperscript{[29]} \textsuperscript{1}H NMR, 400 MHz DMSO: \(\delta = 2.5 (p, J = 3.7, 1.8), 13C\textsuperscript{1}H) NMR, 100 MHz DMSO: \(\delta = 39.52), while \textsuperscript{13}P\textsuperscript{1}H) NMR spectra was referenced to H\textsubscript{3}PO\textsubscript{4}. GC-MS analysis was performed using an Agilent 220-MS fitted with a HP-5 column (30 m x 250 mm x 0.25 mm).

Synthesis

1,3-Bis(2,6-diisoproplyphenyl)imidazolium chloride ([IPhCl]) was synthesized following a slightly modified literature procedure.\textsuperscript{[26]} 17.5 g (0.1 mol) 2,6-diisopropylaniline were dissolved in 100 ml ethanol in a round-bottomed flask and 7.00 g (0.05 mol) 40 wt% aqueous glyoxal solution added followed by three drops of formic acid. After stirring the mixture overnight at room temperature, the bright yellow precipitate (bis-imine) was collected on a porous glass filter, washed with cold methanol and dried. Then, 0.938 g (31.2 mmol) paraformaldehyde was transferred to a Schlenk flask under argon and 9.4 ml 4 M HCl in dioxane (37.5 mol) added. The mixture was stirred until the paraformaldehyde was completely dissolved and the solution turned clear. Afterwards, 5.04 g (13.4 mmol) bis-imine was dissolved in 130 ml of THF in another glass filter, washed with cold methanol and dried. Then, 0.938 g (31.2 mmol) paraformaldehyde was transferred to a Schlenk flask under argon and 9.4 ml 4 M HCl in dioxane (37.5 mol) added. The mixture was stirred until the paraformaldehyde was completely dissolved and the solution turned clear. Afterwards, 5.04 g (13.4 mmol) bis-imine was dissolved in 130 ml of THF in another Schlenk flask under argon and cooled to 0 °C. The paraformaldehyde solution was then transferred to the bis-imine solution via cannula, where after the mixture was allowed to heat to room temperature and left stirring overnight. The precipitated white product was finally collected on a porous glass filter, washed with THF and dried. Yield 2.51 g (44 %). \textsuperscript{1}H NMR data corresponded to published data: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 9.88 (s, 1H, N-CH-N), 8.14 (d, J = 1.6, 2H, N-CH-CH-N), 7.57 (t, J = 7.8, 2H, phen-p), 7.35 (d, J = 7.9, 4H, phen-m), \(\delta = 2.44 (sep, J = 6.8, 4H, me-CH-me), 1.25 (dd, J = 4.9, 6.1, 24H, -CH\textsubscript{2})

1,3-Bis(2,6-diisoproplyphenyl)imidazolylidene ([IPh]) was synthesized following a slightly modified published procedure.\textsuperscript{[27]}
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Analysis

Samples of the solvent and IL phases were analyzed by GC-MS and 1H NMR, respectively. Aniline conversion was quantified using the internal standard method with mesitylene as internal standard. 1H NMR spectra were measured in DMSO-d$_6$ and collected with a relaxation time of two times T$_1$. Product yield of diphenylurea and aniline conversion was quantified using the internal standard method with [BMMIM]Cl.

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Ionic Liquid as promotor – Pd-complex systems in combination with imidazolium ionic liquids catalyze the selective oxidative carbonylation of aniline with unprecedented activity under relatively mild conditions. In-situ NMR study of the reaction system led to observation of an only previously suggested Pd-intermediate.

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Page No. – Page No.

Selective Oxidative Carbonylation of Aniline to Diphenylurea with Ionic Liquids