DOI: 10.1002/adsc.200900133

Donor-Stabilized Phosphenium Adducts as New Efficient and Immobilizing Ligands in Palladium-Catalyzed Alkynylation and Platinum-Catalyzed Hydrogenation in Ionic Liquids

Samer Saleh,[a] Elie Fayad,[a] Michèle Azouri,[a] Jean-Cyrille Hierso,[a,]* Jacques Andrieu,[a,]* and Michel Picquet[a]

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB) – UMR 5260 CNRS, 9 avenue Alain Savary, 21078 Dijon, France
Fax: (+33)-3-8039-6098; e-mail: Jean-Cyrille.Hierso@u-bourgogne.fr or Jacques.Andrieu@u-bourgogne.fr

Received: February 26, 2009; Revised: May 7, 2009; Published online: June 30, 2009

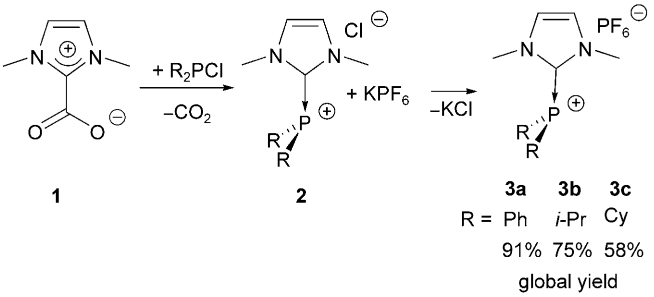
Abstract: The straightforward synthesis of a new donor-stabilized phosphenium ligand **3d** by addition of bromodifurylphosphine to 1,3-dimethylimidazolium-2-carboxylate **1** is described. The obtained ligand exhibits a very strong π-acceptor character, comparable to that of triphenyl phosphite [$P(OPh)_3$] or of tris-halogenophosphines, with a $\nu_{CO}(A_1)$ at 2087 cm^{-1} for its nickel tricarbonyl complex. This ligand, as well as the related **3a** which was obtained from chlorodiphenylphosphine, were tested in palladium-catalyzed aryl alkynylation and in the platinum-catalyzed selective hydrogenation of chloronitrobenzenes, both in an ionic liquid phase. In C–C bond cross-coupling we observed that the increase of the π-acceptor character in ligand **3d**, due to the introduction of an additional electron-withdrawing group, provides a very efficient catalyst in the alkynylation reaction of aryl bromides with phenylacetylene, including the deactivated 4-bromoanisole or the sterically hindered 2-bromonaphthalene. The catalytic activity decreases with recycling due to the sensitiveness of ligands to protonation in the ionic phase. Conversely, a multiple recycling of the metal/ligand system in non-acidic media was achieved from platinum-catalyzed hydrogenation of *m*-chloronitrobenzene. The catalytic results obtained by employing the complex of platinum(II) chloride with **3a** [*trans*-$PtCl_2$(**3a**)$_2$] in comparison with the non-ionic related *trans*-tris(triphenylphosphine)platinum dichloride [*trans*-$PtCl_2(PPh_3)_2$] complex clearly indicate that the simultaneous existence of a strong π-acceptor character and a positive charge within the ligand **3a** significantly increases the life-time of the platinum catalyst. The selectivity of the reaction is also improved by decreasing the undesirable formation of dehalogenation products. This cationic platinum complex *trans*-$PtCl_2$(**3a**)$_2$ is the first example of a highly selective catalyst for hydrogenation of chloronitroarenes immobilized in an ionic liquid phase. The system was recycled six times without noticeable metal leaching in the organic phase, and no loss of activity.

Keywords: catalysis; catalyst recycling; ionic liquids; palladium; phosphenium salts; platinum

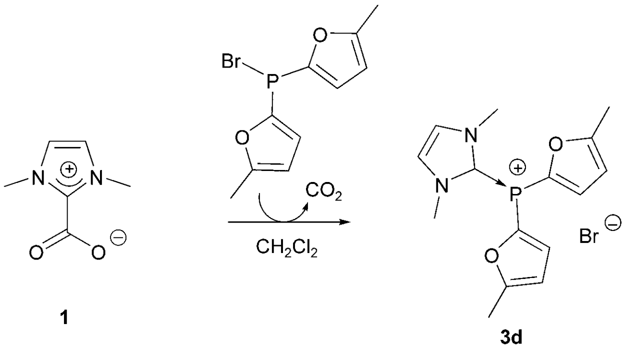
Introduction

In contrast to neutral phosphine ligands, imidazolium-functionalized phosphines represent an interesting opportunity to strongly decrease the metal leaching in homogeneous polyphasic catalysis, especially when using an ionic liquid phase.[1–4] Among these cationic ligands, the imidazolium-2-phosphines not only lead to very active rhodium catalysts in styrene hydroformylation[1] or to palladium complexes able to catalyze the Heck reaction[5] but also represent rare examples of base donor-π-acceptor adducts involving an electron-rich P(III) center as Lewis acceptor.[6] However, the access to a large library of imidazolium-2-phosphines was so far limited to a few examples because of their multistep preparation.[1,7–9] In this context, we have recently described a simple and straightforward synthesis of imidazolium-2-phosphines **2** and **3** by addition of monochlorophosphines to the dimethylimidazolium-2-carboxylate **1** (see Scheme 1).[10] Besides, this synthesis provides access to new dicationic or mixed halide donor-stabilized phosphenium adducts by extension of the reactivity of **1** towards others chlorophosphines.[11]

Moreover, the measurement of the A_1 symmetric stretching frequency of the related $Ni(CO)_3$(**3a–c**) complexes has shown that the ligands **2** and **3** behave as phosphite-like strong π-acceptors. This unexpected



Scheme 1.



Scheme 2.

result is the consequence of the C→P bond in imidazolium-2-phosphines which displaces the formal positive charge from the imidazolium ring to the phosphorus center. Since the combination of this electronic property with an ionic nature renders such ligands very promising in the development of new continuous-flow polyphasic catalytic processes, we describe in this paper, firstly, the extension of our method to a stronger π-acceptor ligand than **3a–c** by addition of bis(5-methyl-2-furyl)bromophosphine to the imidazolium 2-carboxylate **1** and, secondly, the catalytic properties of some obtained complexes in palladium and platinum catalysis in an ionic liquid phase with a particular attention on the recycling opportunities for the future development of continuous flow catalytic processes.

Results and Discussion

By the use of the procedure previously described for **2a–c**, the bromodifurylphosphine slowly reacts with a slight excess of imidazolium 2-carboxylate **1** in CH_2Cl_2 at room temperature (see Scheme 1). The mixture was stirred two days and a light-brown solid was obtained after removal of solvent (Scheme 2).

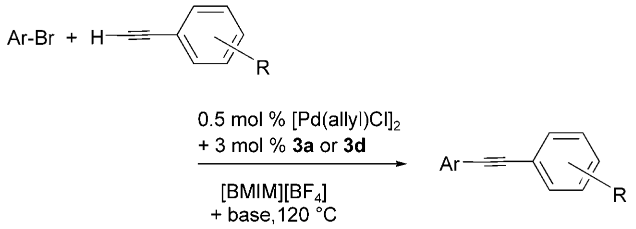
The phosphorus NMR spectrum of this crude product showed the presence of residual bis(5-methyl-2-furyl)bromophosphine, which was easily eliminated by simple washing with diethyl ether. Compound **3d** was identified by the intense resonance detected at −78.9 ppm. The formation of the phosphorus-carbon bond between the N-heterocycle and the phosphorus atom was confirmed by the presence of a doublet at 141.39 ppm in the ^{13}C NMR spectrum, with a typical coupling constant $^{1}J_{P,C}$ of 47 Hz.[10,11] This observation, combined with a 2:1 ratio for furyl *versus* imidazolium groups in its proton NMR spectrum, unambiguously proved the formation of the expected ligand **3d.**

The electron donor properties of the phosphorus atom of a tertiary phosphine are easily evaluated by infrared measurement of the A_1 symmetric stretching frequency detected in the corresponding nickel carbonyl complex prepared *in situ* by phosphine substitution of a CO group in $[Ni(CO)_4]$. Although less toxic compounds than $Ni(CO)_4$ (prepared *in situ* from $[Ni(COD)_2]$) are now more commonly used (such as $[Rh(CO)_2Cl]_2$), we opted to prepare the nickel carbonyl adduct in order to compare easily the parameters of the new imidazolium-2-phosphane complexes directly with the large database tabulated by Tolman[12] and with our other nickel tricarbonyl phosphenium complexes $[Ni(CO)_3(\mathbf{3a–c})]$.[10] Thus, after addition of **3d** to an equimolar amount of $Ni(CO)_4$ in a toluene/CH_2Cl_2 solution, the related $\nu_{CO}(A_1)$ stretching wave number was observed at 2087 cm^{-1} in the infrared spectrum. This higher value categorizes **3d** as being much less electron-donating than the common aryl tertiary phosphines [$\nu_{CO}(A_1) = 2069\ cm^{-1}$ with PPh_3] and more precisely in the range of the tris-halogenophosphines, or of the weaker electron-donating phosphites like $P(OPh)_3$ (2085 cm^{-1}) and $P(OCH_2CH_2CN)_3$ (2088 cm^{-1}).[12] This result is due to the shift of positive charge from the imidazolium ring to the phosphorus, which is consistent with the description of **3a–d** as having a donor-stabilized phosphenium structure instead of the imidazolium-2-phosphine. Nevertheless, their coordination properties remain identical to those reported with phosphine or phosphite ligands in Pt, Pd or Rh chemistry. This new class of ligands is therefore of fundamental and applied interest in molecular catalysis with late transition metals.[10,13,14] Herein, we have further investigated their properties in two different catalytic reactions: namely the palladium-catalyzed aryl alkynylation of aryl bromides and the platinum-catalyzed hydrogenation of nitrobenzenes.

Palladium-Catalyzed Aryl Alkynylation in an Ionic Liquid: Immobilization and Recycling

The palladium-catalyzed cross-coupling reaction between sp^2-hybridized carbon aryl halides and sp-hybridized carbon terminal acetylenes is a very important development in the field of alkyne chemistry since conjugated alkynes are recurring building blocks in bioactive natural products, and in a wide range of industrial intermediaries (pharmaceuticals, agrochemicals), or in molecular materials for optics and electronics.[15] This kind of cross-coupling reaction is efficiently conducted in the combined presence of palladium and a copper salt (mostly CuI) as co-catalyst (Sonogashira reaction). Under certain conditions, the reaction can be conducted with palladium in the absence of copper (Heck alkynylation); this alternative is clearly valuable from a sustainability and economical point of view. Even more interesting is the development of immobilized catalytic systems which opens the way to recycling or continuous-flow chemistry. As a consequence, the potential of the catalytic systems combining [palladium/**3a** (or **3d**)/base] in [BMIM][BF_4] was explored for aryl alkynylation. It has been previously shown that aryl bromides (substrates cheaper and more accessible than iodides but more challenging due to the stronger C–X bonding) can be efficiently used in aryl alkynylation in an ionic liquid.[16,17] The system [Pd/3 PPh_3] (1 mol%) in [BMIM][BF_4] is efficient for the coupling of a variety of activated and deactivated aryl bromides to phenylacetylene; however the recycling was limited by detrimental leaching of the monophosphine ligand throughout the extraction process with organic solvents. We thus decided to explore the potential of the less lipophilic charged donor-stabilized phosphenium adducts in aryl alkynylation reactions. We employed the catalytic systems combining palladium and the catalysis auxiliaries **3a** and **3d** in the presence of pyrrolidine as an organic base (Scheme 3). After preliminary investigation of general reaction conditions (temperatures varied from 80 to 130 °C, and experiment time between 2 and 40 h) we determined suitable conditions to be around 120 °C for 20 h. The inorganic carbonate K_2CO_3 was found to be inefficient in [BMIM][BF_4].

Under these conditions, comparative studies were conducted on four aryl bromides with different steric and electronic features: the activated electron-poor 4-bromoacetophenone, the deactivated electron-rich 4-bromoanisole, the *ortho*-substituted electronically deactivated 2-bromotoluene and the sterically hindered 2-bromonaphthalene. The results are summarized in Figure 1.



Scheme 3.

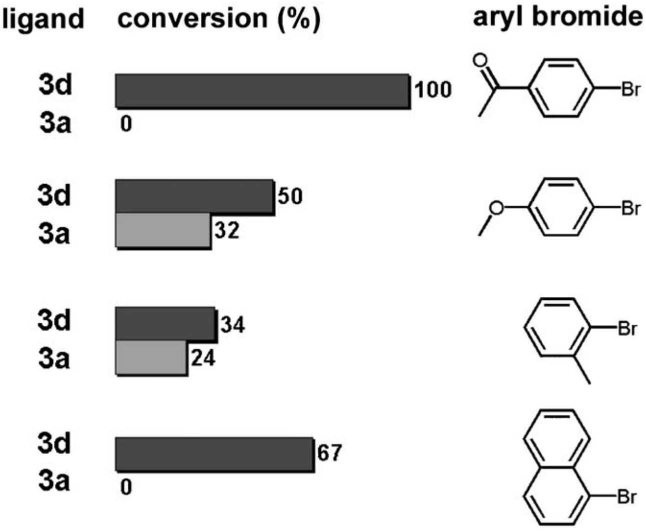
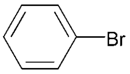
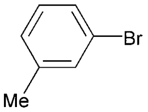
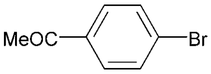
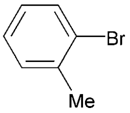
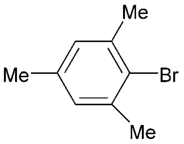
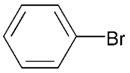
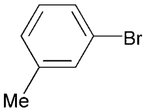
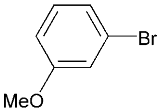
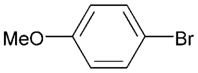


Figure 1. Effect of the stronger π-acceptor ligand on palladium alkynylation of different aryl bromides in [BMIM][BF_4].

Under these conditions, the palladium precursor combined with **3d** was found to be a superior system, in all cases, than the analogous palladium complex containing **3a**, in terms of activity and reproducibility of results. For instance, the coupling of 4-bromoacetophenone and 2-bromonaphthalene to phenylacetylene was problematic with **3a**, while [Pd/**3d**] gave good to high yields of coupling products (67–100%) (see Figure 1). A less clear cut result was found with the electronically deactivated substrates 4-bromoanisole and 2-bromotoluene since for both ligands only 24 to 50% conversions were obtained.

Based on these preliminary indications, the catalytic investigations and optimization were focused on the system incorporating **3d**. Table 1 summarizes the scope and limitation of the [Pd/**3d**/pyrrolidine] catalytic system for phenylacetylene arylation in [BMIM][BF_4], together with the recycling runs conducted from the best conversions. Under the optimized conditions, and in the noticeable absence of CuI co-catalyst, complete arylation of phenylacetylene were performed from bromobenzene, 3-bromotoluene and 4-bromoacetophenone (quantitative yields, entries 1–3). Good to moderate coupling was also obtained from 3-bromoanisole (82% yield, entry 8), 4-bromoanisole (58% yield, entry 9) and 2-methylbromobenzene (50% yield, entry 4), indicating that either strongly unfavorable electronic or steric effects slightly hamper the performances of the system. However, the catalyst activity was clearly limited for the conversion of the trisubstituted 2-bromomesitylene (both electronically and sterically deactivated) even over a long reaction time (entry 5, 26% yield of coupling

Table 1. Palladium-catalyzed alkynylation with various aryl bromides in [BMIM][BF_4].

Entry	Aryl Bromide	Conditions *Tp* [°C]/*t* [h]	Run 1 Yield [%][a]	1st Recycling Yield [%][a]	2nd Recycling Yield [%][a]
1		125/40	99 (90)	99	60
2		125/40	99 (95)	60	40
3		90/40	99 (90)	75	
4		125/40	50		
5		125/48	26		
6		125/40	95 (85)	70[b]	
7		125/40	95 (85)	40[b]	
8		125/40	82	32[b]	
9		125/40	58		

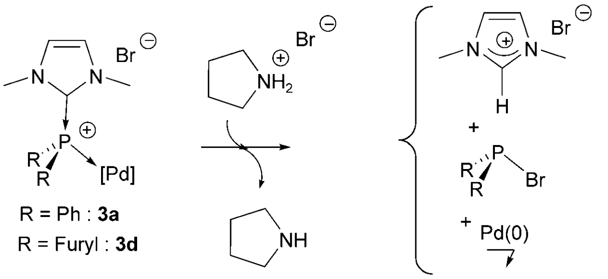
[a] Yields based on aryl bromides (average of two runs), determined by GC (external standard); isolated yields obtained after chromatography on silica column reach 90 to 95% of these values; isolated yields are in brackets.

[b] In these recycling experiments $NaNH_2$ was employed to regenerate the pyrrolidine base.

after 48 h), under similar conditions [Pd/3 PPh_3] gave a complete conversion.[17]

After ethereal extraction of the coupling product under argon, the resulting ionic liquid phase was reused without any pre-treatment and refilled with the coupling reagents and the pyrrolidine base (1st recycling, entries 1–3). While the recycling of bromobenzene gave excellent results (99% yield), functionalized aryl bromides such as 3-bromotoluene and 4-bromoacetophenone showed a drop of activity (60 and 75% yield, respectively). A second recycling confirmed this tendency (see Table 1). ^{31}P NMR experiments on the extracted phases did not point out any traces of ligand leak into the organic phase, in contrast to experiments where triphenylphosphine was employed as ligand.[17] However, careful ^{31}P NMR experiments conducted over long periods of time on concentrated ethereal phases after recycling were informative to understand the origin of the deactivation of the immobilized catalytic systems. From extraction after experiments using the ligand **3d**, the ^{31}P NMR signature of bis(5-methyl-2-furyl)bromophosphine and its corresponding phosphine oxide was unambiguously detected (singlets at 1.7 and 15.9 ppm in $CDCl_3$, respectively). Scheme 4 depicts a reasonable pathway to explain the formation of these phosphine products and the presence of inactive palladium(0).

Due to the specific features of the donor-stabilized phosphenium adducts[10] the accumulation of a large excess of acidic pyrrolidinium bromide would be conducive to the C→P bond cleavage through the protonation of the carbenic 1,3-dimethylimidazol-2-ylidene of the ligand at the relatively high temperatures employed. The concomitantly formed phosphine halide being oxygen-sensitive, a mixture of the phosphine and its phosphine oxide is detected in the NMR spectra. We thus believe that the large excess of pyrrolidinium bromide could be at the origin of the system's



Scheme 4. Acidic deactivation pathway proposed for [Pd/**3a,d**] catalytic systems.

deactivation. As a consequence we looked for an elegant method to overcome these troubles upon recycling. A possible approach was investigated, founded on the successful coupling of bromobenzene, 3-bromotoluene and 3-bromoanisole (run 1, entries 6–8). The strategy aimed at the regeneration of the pyrrolidine base by addition of $NaNH_2$ with simultaneous elimination of the acidic protons in the form of the volatile ammonia.[29] This method eventually allowed a second run as the expected coupling products were obtained in 30 to 70% yield (1st recycling, entries 6–8). However, the course of the reaction was seriously hampered by the formation of residual NaBr that produces a very viscous mixture which is certainly at the origin of mass-transfer problems.

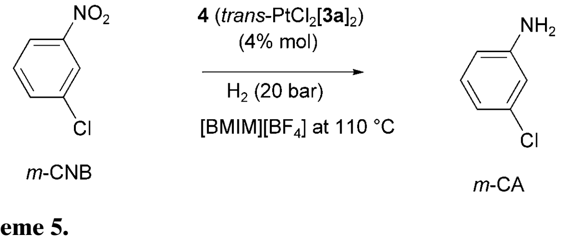
The present catalytic investigations have thus proved the potential of imidazolium phosphines as ligands in the copper-free palladium-catalyzed alkynylation of aryl bromides. From a general point of view the selectivity towards the expected coupling product is good to excellent; nevertheless room of progress is possible in terms of activity of the immobilized system and its stability towards acidic attack. In order to avoid this problem of incompatibility of such ligands in catalyses performed in acidic media, we transferred our interest to another important catalytic reaction which does not generate acidic protons, such as the platinum-catalyzed hydrogenation of nitrobenzenes with ligands **3**.

Platinum-Catalyzed Hydrogenation in an Ionic Liquid: Immobilization and Recycling

The catalytic hydrogenation of halonitrobenzenes to the corresponding haloanilines without detrimental dehalogenation is an exciting challenge due to their several applications in the manufacture of herbicides, pesticides or chemical fertilizers.[18] Since the discovery of a ruthenium phosphine complex as catalyst for these hydrogenation reactions,[19] different transition metal complexes have been examined with the view to get haloaminobenzenes without by-products resulting from dehalogenation or cross-coupling reactions.[20–24] For instance, with d^8-transition metals, Pd/C was found to be an efficient and selective catalyst,[20] while characterization of such catalyst at the molecular state remains troublesome. For sustainable chemistry development, ionic liquids are attracting much interest in catalytic transformations as they can have a profound effect on activity and selectivity. Indeed a carbon-supported platinum system in ionic liquids has been shown to be more active than the analogous palladium system or Raney nickel in the hydrogenation of halonitrobenzenes and performs better in the ionic liquid [BMIM][BF_4] than in methanol. Besides, this platinum catalyst affords not only a higher selectivity but can be then recycled more than five times without any apparent decrease of activity and selectivity.[25] It therefore represents, to the best of our knowledge, one of the most relevant catalytic systems for this selective hydrogenation reaction without any equivalent in homogeneous catalysis. Due to the good performance of this heterogeneous Pt/C system in ionic liquids, we have thus examined the catalytic properties of our air-stable cationic donor-stabilized phosphenium Pt(II) complex in the homogeneous catalyzed hydrogenation of chloronitrobenzenes (CNB) to chloroanilines (CA) in an ionic liquid, anticipating that the presence of the cationic imidazolium moiety should inhibit an eventual metal leaching into the extracting non-polar organic phase.

A first catalytic experiment was carried out with the platinum complex **4** *trans*-$PtCl_2$[**3a**]$_2$ in the presence of 25 equivalents of *m*-CNB in 10 mL of [BMIM][BF_4] under 20 bars of hydrogen at 110 °C during 48 h (See Scheme 5).

After ethereal extraction of the organic products, the related GC analysis exhibited a complete conversion of *m*-CNB to *m*-CA and only traces of aniline (<0.5%). We then performed a kinetic monitoring of the reaction and found that the conversion increased with time from 55% after 4 h to 63% and 100%, respectively after 18 and 48 h. This diminution of the reaction rate after 4 h could be a significant indication of a poisoning of the catalyst by the *m*-CA formed. Thus, while our donor-stabilized phosphenium platinum complex led to a high selectivity, which maintains the dehalogenation reaction to a lower level, the activity remained lower than that of the Pt/C heterogeneous catalyst.[25] However, care should be taken in



Scheme 5.

this comparison because of the different dilution conditions used in this study, particularly regarding the substrate which is forty times more diluted in the present molecular system (see Experimental Section).

Additional catalytic experiments were performed under conditions identical to the ones described above with variation of the nature of CNB and the ligand. The donor-stabilized phosphenium platinum complex remained totally inactive in hydrogenation of *o*-CNB while only little difference has been pointed out with Pd/C[20] or Pt/C.[25] Conversely, a partial conversion of 85% was observed with the analogous bis-(triphenylphosphine)dichloroplatinum complex **5**. This latter observation shows the very strong influence of π-acceptor character in phosphorus ligands on the platinum catalytic activity.

Since our donor-stabilized phosphenium platinum catalyst exhibited an unprecedented selectivity in conversion of *m*-CNB to *m*-CA in homogeneous phase, we evaluated its potential in recycling processes. After 48 h, the organic compounds were extracted from [BMIM][BF_4] several times with diethyl ether under an inert atmosphere. The ionic liquid phase was then reloaded with *m*-CNB (substrate to catalyst ratio = 25) before being reintroduced into the autoclave. The catalytic conditions described for the first catalytic run were then applied to the new catalytic mixture. After the recycling, the ionic liquid was recovered and reused for a further catalytic experiment using the above procedure until the sixth recycling. The conversion of *m*-CNB to *m*-CA and the amount of undesirable dehalogenation product for each catalytic run are summarized in Figure 2.

It is noteworthy that the activity remained constantly high (between 94 and 100%) even after seven catalytic runs, corresponding to a cumulative TON of 167. The selectivity was also remarkable with a weak dehalogenation level, the amount of aniline starting only to be detectable from the fourth recycling and reaching a maximum of only 2.3% at the seventh recycling (see Figure 2).

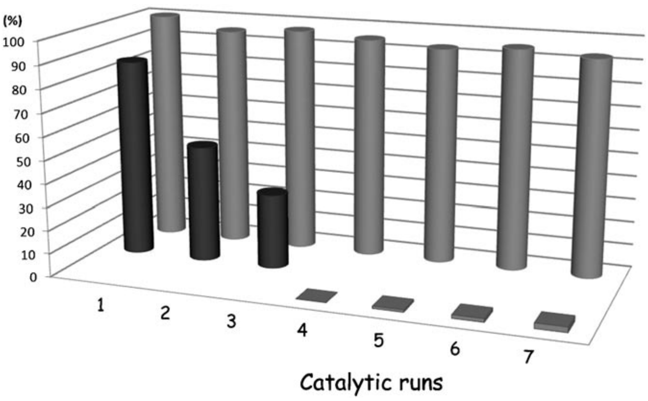


Figure 2. Pt-catalyzed hydrogenation results of *m*-CNB with the recovered ionic liquid phase. % conversion of *m*-CNB to *m*-CA with platinum complexes **4** (● in the background) and **5** (● in the foreground) and % aniline formed with platinum complex **4** (■). Yields were determined by GC.

These excellent catalytic performances have then been compared to those found with its neutral triphenylphosphine platinum analogue **5** *trans*-$PtCl_2(PPh_3)_2$ and are given in Figure 2. In contrast to complex **4**, only a partial conversion of 85% was observed with a rapid decrease down to 32% at the second recycling, that is, a global TON = 42 for complex **5** after three runs whereas complex **4** performed a TON = 73.5 at the same stage. Additionally, this neutral complex showed from the first catalytic run a poor selectivity with the formation of 5% of dehalogenated aniline and the presence of a significant amount of insoluble zero-valent metal which is the consequence of rapid catalyst deactivation. We believe that such differences in activity and selectivity between the platinum catalysts **4** and **5** are directly linked to the cationic nature and structure of the coordinated phosphorus ligand **3a**. Indeed, in contrast to the triphenylphosphine ligand, the positive charge present in ligand **3a** makes it insoluble in diethyl ether and no ligand leaching from the ionic liquid phase occurs during the extraction process. The catalyst that remains in the ionic liquid solution is therefore stabilized while it rapidly decomposes if the ligand is extracted such as in the case of PPh_3. This is consistent with the absence of insoluble zero-valent metal in the case of complex **4**. The outstanding life-time of this platinum complex, without significant loss of activity after a total of 14 days at 110 °C, also shows unambiguously the robustness of the donor-stabilized phosphenium ligands, provided no acidic protons are used or formed during the reaction as previously shown in the palladium alkynylation reaction. Moreover, it should be pointed out that the recycling experiments performed here prove also the robustness of ligand **3a** towards water which is co-produced during the hydrogenation catalytic cycle.

Conclusions

The results reported herein clearly demonstrate the utility of donor-stabilized phosphenium adducts in late transition metal catalysis. The introduction of an additional electron-withdrawing group like furyl in the cationic ligand allowed us to decrease even more its already weak basicity and led to a very efficient palladium catalyst in the alkynylation reaction of various aryl bromides, including weakly reactive substrates. Although the catalyst remained insoluble in non-polar organic solvents and was thus successfully immobilized in the IL phase during recycling attempts, its activity in [BMIM][BF_4] decreased from the first recycling. The deactivation was found to be due to a protonation reaction of the C→P bond of the ligand in the presence of the large quantity of pyrrolidium salt formed upon the successive recycling. This observation suggests a certain incompatibility of such ligands with catalytic reactions performed in acidic media, or which generate easily transferred protons, especially when no treatments are done on the reused phase (water washing, etc.). Conversely, the catalytic results obtained with the *trans*-$PtCl_2(\mathbf{3a})_2$ complex compared to its related neutral complex *trans*-$PtCl_2(PPh_3)_2$ in the hydrogenation of chloronitrobenzenes in [BMIM][BF_4] confirmed the recycling potential of donor-stabilized phosphenium ligands. The simultaneous existence of a strong π-acceptor character and a positive charge in the phosphorus ligand substantially improved the life-time of the platinum catalyst. The chemical selectivity of the reaction was also eventually increased by suppressing the detrimental formation of the dehalogenation product. Therefore, this cationic platinum complex represents, to the best of our knowledge, the first example of highly selective homogeneous catalyst for the reduction of nitroarenes in an ionic liquid phase. The platinum catalytic system was successfully recycled seven times without noticeable metal leaching in the organic phase and any significant loss of activity.

Experimental Section

General Procedures

All reactions were performed in Schlenk-type flasks under an argon atmosphere except hydrogenation experiments which were performed in a Parr 300-mL stainless steel autoclave equipped with a magnetic drive and an internal glass vessel. The temperature was controlled by a rigid heating mantle and by a single loop cooling coil. Solvents were purified and dried by conventional methods and distilled under argon. Chromatography was performed on silica gel (230–400 mesh, Merck Kieselgel 60). GC and GC-MS analyses were performed in our Laboratories on Shimadzu GC-2014 with a Supelco Equity-5 capillary column (30 m × 0.25 mm × 0.25 μ), Hewlett–Packard HP-6890 series with a HP-5 capillary column (30 m × 0.25 mm × 0.25 μ) and ThermoFinnigan TRACE GC with a RTX-5 capillary column (5 m × 0.25 mm × 0.25 μ) and an UltraFast module. GC yields are based upon external standard calibration from pure starting substrates and reaction products. The program used in GC-MS and GC for experiments was the following: carrier gas He, gas flow 1.3 $mL\,min^{-1}$; injector 300 °C, oven temperature program: 1 min at 60 °C, 20 °Cmin^{-1} till 280 °C, 5, 10 or 15 min at 280 °C, detector FID 300 °C or MSD; the program used in UltraFast GC for experiments was the following: carrier gas H_2, gas flow 0.3 $mL\,min^{-1}$; injector 250 °C, column program: 6 sec at 50 °C, 200 °Cmin^{-1} till 200 °C, isotherm at 200 °C, detector FID 250 °C. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K on a Bruker Avance 300 spectrometer. All chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR) and are given in ppm. The elemental analyses were performed in our Institute on a Fisons EA 1108 apparatus. The $[Pd(allyl)Cl]_2$, $PtCl_2(PPh_3)_2$ **5**, bromoaryles, phenylacetylene, *m*-CNB and *o*-CNB were commercial products and were used as received. The bis(5-methyl-2-furyl)bromophosphine, 1,3-dimethylimidazolium 2-carboxylate **1**, donor-stabilized phosphenium **3a**, $PtCl_2(\mathbf{3a})_2$ **4**, and ionic liquid [BMIM][BF_4] were prepared according to the literature.[10,26–28] The solids (catalyst and reagents) and the ionic liquid were degassed under vacuum before use.

Synthesis of Donor-Stabilized Phosphenium Adduct 3d

To a suspension of 1,3-dimethylimidazolium 2-carboxylate **1** (0.216 g, 1.54 mmol) in CH_2Cl_2 (5 mL) was very slowly added the bis(5-methyl-2-furyl)bromophosphine (0.488 g, 1.79 mmol). A purple colour appeared immediately which slowly changed to light brown after 18 h of stirring. The mixture was stirred for two days at room temperature. The solvent was removed under vacuum to afford a light brown solid which was washed twice with 5 mL of degassed pentane and ether, and dried under vacuum; yield: 0.539 g (95%); mp 131 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.28$ (s, 2H, N-CH=CH-N), 6.88 (s, 2H, $H_{3\ furyl}$), 6.09 (m, 2H, $H_{4\ furyl}$), 3.94 (s, 6H, NCH_3), 2.32 (s, 6H, $CH_{3\ furyl}$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 160.81$ (d, $J_{P,C} = 2.3$ Hz, 2C, $C_{2\ furyl}$), 141.39 (d, $J_{P,C} = 47.0$ Hz, 1C, NCN), 138.24 (s, 2C, $C_{5\ furyl}$), 127.60 (s, 1C, N-CH=), 127.13 (s, 1C, N-CH=), 123.39 (d, 2C, $C_{4\ furyl}$), 108.57 (d, $^3J_{P,C} = 8.3$ Hz, 2C, $C_{3\ furyl}$), 37.46 (d, $^3J_{P,C} = 8.3$ Hz, 2C, NCH_3), 13.98 (d, $^4J_{P,C} = 19.6$ Hz, 2C, $CH_{3\ furyl}$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -78.9$ (s); anal. calcd. for $C_{15}H_{18}N_2O_2PBr$ (368.02): C 48.90, H 4.93, N 7.61; found: C 48.37, H 4.91, N 7.91.

Representative Catalytic Experiment for the Heck Alkynylation Reaction in [BMIM][BF_4]

The solid mixture of $[Pd(allyl)Cl]_2$ (6.3 mg, 0.0348 mmol of Pd), donor-stabilized phosphenium (**3a**: 32 mg, 0.102 mmol or **3d**: 38 mg, 0.102 mmol) and bromobenzene (0.358 mL, 536 mg, 3.416 mmol) was degassed for 15 min in a 20-mL Schlenk tube equipped with a magnetic stirrer bar. Under argon were added 3 mL of [BMIM][BF_4] previously degassed under reduced pressure for 10 min. The Schlenk tube was heated in an oil bath at 90 °C to give a red-orange solution. To the ionic liquid solution was added, out of the oil bath, 0.35 mL pyrrolidine (1.6 equiv., 390 mg, 5.46 mmol, $d = 0.87$) then 0.60 mL phenylacetylene (1.6 equiv., 558 mg, 5.46 mmol, $d = 0.93$). The resulting mixture was heated at 125 °C for 40 h under argon. The product was extracted from the ionic liquid phase by the addition of diethyl ether (two times 5 or 10 mL) and decanting off the ether from the ionic liquid phase (GC yield: 99%). After evaporation the residue was purified by silica gel chromatography (diethyl ether/hexane: 1/9) to give (2-phenylethynyl)benzene; isolated yield: 540 mg (90%).

The products obtained were analysed by proton NMR, mass spectrum analysis and elemental analysis, and were found identical to commercial products.

Recycling Experiment for the Heck Alkynylation Reaction in [BMIM][BF_4]

After extraction with diethyl ether under argon the resulting dark coloured ionic liquid was reused without any specific treatment, but was degassed under reduced pressure for 15 min. The aryl halide was added and the mixture degassed for 15 min. The reaction was carried out after addition of pyrrolidine and phenylacetylene and work-up was done under the same conditions as employed for the first run.

Catalytic Hydrogenation Experiments with Platinum Complexes

The autoclave was purged three times under vacuum/argon before introduction of the catalytic solution. The reactor was charged with **4** [*trans*-$PtCl_2$(**3a**)$_2$: 21 mg, 1.857×10^{-2} mmol] or **5** [*trans*-$PtCl_2(PPh_3)_2$: 15 mg, 1.857×10^{-2} mmol], *m*- or *o*-chloronitrobenzene (71 mg, 0.45 mmol) and 10 mL of [BMIM][BF_4] and then heated at 110 °C. When the desired temperature was reached, the reactor was filled with 20 bars of hydrogen and the mixture was stirred for 48 h. The reactor was cooled until room temperature and the organic products were extracted with diethyl ether and then analyzed by Ultrafast GC.

The identification of the organic compounds was performed by comparison with pure commercial compounds.

Acknowledgements

We wish to acknowledge the Ministère de l'Enseignement Supérieur et de la Recherche for support and for PhD fellowship to S. S. and M. A. We also thank the Université de Bourgogne, the Centre National de la Recherche Scientifique and the "Conseil Régional de Bourgogne" for financial support of this work.

References

[1] D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, *J. Organomet. Chem.* **2001**, *630*, 177–184.
[2] S.-G. Lee, Y. J. Zhang, J. Y. Piao, C. E. Song, J. H. Choi, J. Hong, *Chem. Commun.* **2003**, 2624–2625.
[3] R. P. J. Bronger, S. M. Silva, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Dalton Trans.* **2004**, 1590–1596.
[4] J. Andrieu, M. Azouri, *Inorg. Chim. Acta* **2007**, *360*, 131–135.
[5] Q.-X. Wan, Y. Liu, Y. Lu, M. Li, H.-H. Wu, *Catal. Lett.* **2008**, *121*, 331–336.
[6] B. D. Ellis, P. J. Ragogna, C. L. B. Macdonald, *Inorg. Chem.* **2004**, *43*, 7857–7867.
[7] A. A. Tolmachev, A. A. Yurchenko, A. S. Merculov, M. G. Semenova, E. V. Zarudnitskii, V. V. Ivanov, A. M. Pinchuk, *Heteroat. Chem.* **1999**, *10*, 585–597.
[8] I. V. Komarov, M. Y. Kornilov, *Tetrahedron* **1995**, *51*, 11271–11280.
[9] N. Kuhn, J. Fahl, D. Bläser, R. Boese, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729–734.
[10] M. Azouri, J. Andrieu, M. Picquet, P. Richard, B. Hanquet, I. Tkatchenko, *Eur. J. Inorg. Chem.* **2007**, *31*, 4877–4883.
[11] M. Azouri, J. Andrieu, M. Picquet, H. Cattey, *Inorg. Chem.* **2009**, *48*, 1236–1242.
[12] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[13] N. Kuhn, M. Goëhner, G. Henkel, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1415–1416.
[14] J. Andrieu, M. Azouri, P. Richard, *Inorg. Chem. Commun.* **2008**, *11*, 1401–1404.
[15] H. Doucet, J.-C. Hierso, *Angew. Chem.* **2007**, *119*, 850–888; *Angew. Chem. Int. Ed.* **2007**, *46*, 834–871.
[16] J.-C. Hierso, M. Picquet, H. Cattey, P. Meunier, *Synlett* **2006**, 3005–3008.
[17] J.-C. Hierso, J. Boudon, M. Picquet, P. Meunier, *Eur. J. Org. Chem.* **2007**, *4*, 583–587.
[18] P. J. Chenier, *Survey of Industrial Chemistry*, 2nd revised edn., VCH, Weinheim, **1992**.
[19] J. F. Knifton, *J. Org. Chem.* **1976**, *41*, 1200–1206.
[20] V. Kratky, M. Kralik, M. Mecarova, M. Stolcova, L. Zalibera, M. Hronec, *Appl. Catal. A* **2002**, *235*, 225–231.
[21] A. Corma, P. Sema, P. Concepción, J. J. Calvino, *J. Am. Chem. Soc.* **2008**, *130*, 8748–8753.
[22] P. Maity, S. Basu, S. Bhaduri, G. K. Lahiri, *Adv. Synth. Catal.* **2007**, *349*, 1955–1962.
[23] N. Maity, P. R. Rajamohanan, S. Ganapathy, C. S. Gopinath, S. Bhaduri, G. K. Lahiri, *J. Phys. Chem. C* **2008**, *112*, 9428–9433.
[24] F. Cárdenas-Lizana, S. Gómez-Quero, M. A. Keane, *Appl. Catal. A* **2008**, *334*, 199–206.
[25] D.-Q. Xu, Z.-Y. Hu, W.-W. Li, S.-P. Luo, Z.-Y. Xu, *J. Mol. Catal. A* **2005**, *235*, 137–142.
[26] J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet, M. Santelli, *Tetrahedron* **2005**, *61*, 9759–9766.
[27] M. Picquet, D. Poinsot, S. Stutzmann, I. Tkatchenko, I. Tommasi, P. Wasserscheid, J. Zimmermann, *Top. Catal.* **2004**, *29*, 139–143.
[28] P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. De Souza, J. Dupont, *Polyhedron* **1996**, *15*, 1217–1219.
[29] While this work was in progress, Wan et al. reported a similar strategy using aqueous NaOH treatement to recover the free amine in a Heck reaction, see ref.[5]