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Highly efficient aqueous phase chemoselective hydrogenation of α,β-unsaturated aldehydes catalysed by phosphine-decorated polymer immobilized IL-stabilized PdNPs†‡

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Phosphino-decorated polymer immobilised ionic liquid phase stabilised palladium nanoparticles (PdNP@PPh$_2$-PIILP) and their PEGylated counterparts (PdNP@PPh$_2$-PEGPIILP) are remarkably active and exceptionally selective catalysts for the aqueous phase hydrogenation of α,β-unsaturated aldehydes, ketones, esters and nitriles with PdNP@PPh$_2$-PEGPIILP giving complete conversion and 100% selectivity for reduction of the C═C bond, under mild conditions. This is the most selective PdNP-based system to be reported for the aqueous phase hydrogenation of this class of substrates.

Ionic liquids are an intriguing class of solvents that have been widely used in catalysis as a result of their low vapour pressure, chemical and thermal stability, wide electrochemical window, excellent solvation properties and potential green credentials.[1] In particular, their dual role as both a solvent and stabilizer, and the ability to modify and tune their physiochemical properties and functionality, has fuelled their development in the synthesis of metal nanoparticles for use in catalysis.[2] Even though there has been considerable progress in this area and our understanding of these systems is now reasonably well-advanced, the use of ionic liquids suffers a number of practical limitations including their high cost compared with traditional solvents, high viscosity, leaching of the ionic liquid during work-up and recovery and aggregation of metal nanoparticles under catalytic conditions.

The concept of supported ionic liquid phase (SILP) catalysis was introduced to reduce the volume of ionic liquid required and facilitate catalyst separation and recovery.[3] However, these systems suffer drawbacks such as pore blocking and leaching of ionic liquid and/or catalyst. In a more recent development, ionic liquids have been covalently immobilised on to polymers, either as a single or multi-layer, which further reduces the amount of ionic liquid and prevents leaching while retaining the advantageous properties of an ionic liquid environment such as catalyst stabilisation, facile catalyst activation, enhancements in rate and selectivity and efficient recyclability.[4] In this regard, there have been numerous successful applications of this strategy to the immobilisation and stabilisation of metal nanoparticles. Examples include aqueous phase Suzuki–Miyaura coupling and Heck reactions with multi-layered supported ionic liquid phase palladium nanoparticles[5,6] as well as tris-imidazolium salt-stabilised PdNPs,[7] carbonylative Suzuki–Miyaura coupling with supported ionic liquid phase-stabilised PdNPs,[8] Heck reactions catalysed by palladium immobilised on a gel-supported ionic liquid-like phase,[9] selective hydrogenations with ion exchange resin stabilised PdNPs[10] and aqueous phase oxidation of 1-phenylethanol with SIILP-stabilised gold nanoparticles.[11]

The stabilisation of nanoparticles by ionic liquids has been thoroughly explored and is believed to result from weak electrostatic interactions that are easily displaced to generate the active site.[12] However, while these interactions must be efficiently displaced to achieve high activity they are often not sufficient to prevent nanoparticle aggregation under the conditions of catalysis. One potential solution to this problem has been to incorporate a metal-binding heteroatom donor group such as an amine,[13] nitrile,[14] thiolate,[15] bipyridine,[16] hydroxyl[17] or phosphine[18] on to the ionic liquid on the basis that an additional covalent interaction will improve the long-

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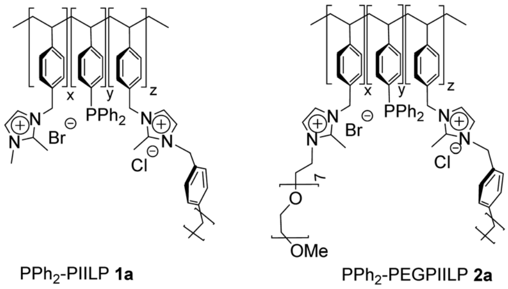
† This paper is dedicated to the memory of Professor Malcolm H. Chisholm (FRS).

‡ Electronic supplementary information (ESI) available: Synthesis and characterisation of imidazolium-based monomers, co-polymers **1a–4a**, PdCl$_4$-loaded co-polymers **1b–4b** and polymer immobilised ionic liquid stabilised PdNPs **1c–4c**; TGA and DSC curves for **2a–c** and **3a–c**, SEM images of **1a–4a**, **1b–4b** and **1c–4c**, TEM images of **1c–4c**, FTIR traces and X-ray photoelectron spectra of **1b–4b** and **1c–4c**. See DOI: 10.1039/c6gc03528k

term stability of the nanoparticles and/or control the kinetics of nanoparticle formation. As this approach has been reported to improve stability, solubility, activity and recyclability of NP catalysts we became interested in extending this concept and developing heteroatom donor-decorated polymer immobilised ionic liquids with the intention of combining the favourable properties and characteristics of an immobilised ionic liquid with heteroatom donor functionalisation. Moreover, there may well be additional benefits associated with incorporating heteroatom donors into polymer immobilised ionic liquids arising from changes to the electronic structure of the metal surface and/or hydrophilicity of the ligand environment as the presence of an amino or thiol group has been reported to improve or switch the chemoselectivity of NP-catalysed hydrogenations[19] as has a secondary phosphine oxide[20] and tertiary phosphines;[18a] the former two appear to operate *via* specific noncovalent molecular interactions and the latter *via* a metal–ligand cooperative mechanism. In addition, P-containing ionophilic ligands have been reported to generate smaller PdNPs than when a ligand was not present and the resulting catalysts were markedly more selective for the hydrogenation of 2-pentyne and cyclohexadiene.[18a] Herein we report the first example of phosphino-decorated PIILP-stabilised palladium nanoparticles (PdNP@PPh$_2$-PIILP) and their PEGylated counterparts (PdNP@PPh$_2$-PEGPIILP) and their use as catalysts for the aqueous phase chemoselective hydrogenation of α,β-unsaturated aldehydes and ketones. To this end, the stabilisation of palladium nanoparticles for use in aqueous phase catalysis is currently a burgeoning area of interest as it offers immense potential for developing greener sustainable processes.[21] The nomenclature chosen to describe these polymers and the corresponding NP-loaded systems attempts to identify their composition and/or modification according to Fig. 1. The most noteworthy developments in this project include (i) the highest selectivities to be reported for the aqueous phase PdNP-catalysed hydrogenation of α,β-unsaturated aldehydes with up to 100% selectivity for addition to the C=C bond under mild conditions and (ii) a marked improvement in performance for PEGylated PPh$_2$-decorated polymer immobilised ionic liquid stabilised PdNPs (PdNP@PPh$_2$-PEGPIILP) compared with PdNP@PPh$_2$-PIILP.



Summary of Pd(II) and PdNP-based PIILs

PdCl$_4$@PPh$_2$-PIILP, **1b**; PdCl$_4$@PPh$_2$-PEGPIILP, **2b**
PdNP@PPh$_2$-PIILP, **1c**; PdNP@PPh$_2$-PEGPIILP, **2c**

Fig. 1 Composition and formulation of polymer immobilised ionic liquids **1a–2a** and their $[PdCl_4]^{2-}$ loaded counterparts (**1b–2b**) and PdNP (**1c–2c**).

Phosphino-decorated PIILP **1a** was prepared by AIBN-initiated radical polymerisation of the corresponding imidazolium-modified monomer, dicationic cross-linker and 4-diphenylphosphino styrene in the desired ratio ($x = 1.84$, $y = 1$, $z = 0.16$) and its PEGylated counterpart **2a** was prepared in a similar manner with the intention of introducing additional weak NP-stabilising interactions and improving water solubility for aqueous phase catalysis;[22] full details and the corresponding characterisation data are provided in the ESI.‡

A 1 : 2 ratio of PPh$_2$-based monomer to imidazolium co-monomer and cross-linker was chosen such that complete exchange of halide in polymers **1a** and **2a** for $[PdCl_4]^{2-}$ would correspond to a palladium to heteroatom ratio of one. Thus, both polymers were impregnated with $[PdCl_4]^{2-}$ to afford **1b** and **2b** (**1b**, PdCl$_4$@PPh$_2$-PIILP; **2b**, PdCl$_4$@PPh$_2$-PEGPIILP) as red-brown solids in near quantitative yield; full characterisation data are provided in the ESI.‡ The solid state ^{31}P NMR spectra of PdCl$_4$@PPh$_2$-PIILP **1b** and PdCl$_4$@PPh$_2$-PEGPIILP **2b** confirm the presence of a Pd–P interaction which is clearly evident from the change in the chemical shift from δ −8 and −10 ppm, respectively, to δ 29 and 32 ppm, respectively. The corresponding PIILP-stabilised nanoparticles **1c** and **2c** (**1c**, PdNP@PPh$_2$-PIILP; **2c**, PdNP@PPh$_2$-PEGPIILP) were prepared by sodium borohydride reduction of **1b** and **2b**, respectively, in ethanol and isolated as black powder in good yield. As for **1b** and **2b**, the solid state ^{31}P NMR spectra of **1c** and **2c** do not contain signals associated with uncoordinated PPh$_2$; this suggests that the surface of the palladium nanoparticles is decorated with phosphino groups. TEM analysis showed that **1c** and **2c** consist of small near monodisperse nanoparticles with average diameters of 2.29 ± 0.96 nm (**1c**) and 1.93 ± 0.67 nm (**2c**) (Fig. 2 and the ESI‡), XPS analysis confirmed that

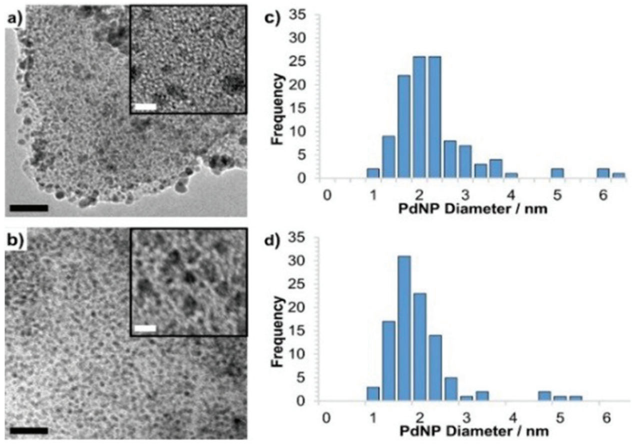


Fig. 2 HRTEM images of (a) PdNP@PPh$_2$-PIILP (**1c**) and (b) PdNP@PPh$_2$-PEGPIILP (**2c**) and particle size distributions determined by counting >100 particles revealing mean NP diameters of 2.29 ± 0.96 nm and 1.93 ± 0.67 nm for (c) **1c** and (d) **2c** respectively. Scale bars are 25 nm (black) and 5 nm (white).

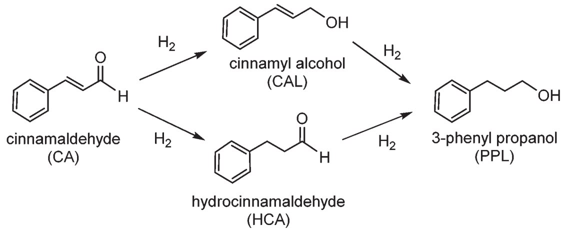


Fig. 3 Reaction pathways for the hydrogenation of *trans*-cinnamaldehyde.

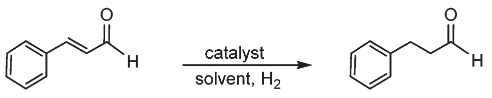
both **1c** and **2c** were composed of mixtures of Pd(II) and Pd(0) and the palladium content was determined by ICP-OES.

The hydrogenation of cinnamaldehyde was identified as an initial benchmark transformation for catalyst evaluation as the products of this reaction are valuable intermediates for the synthesis of fine chemicals, pharmaceuticals and perfumes (Fig. 3).[23] Furthermore, numerous palladium nanoparticle based systems have been reported to be highly selective for hydrocinnamaldehyde and as such will be suitable benchmarks for comparison. For example, palladium-decorated carbon nanotubes/charcoal composites gave hydrocinnamaldehyde in 96% selectivity albeit at a relatively low conversion of 41% as did AuPd on ordered mesoporous carbon (OMC),[24a,b] palladium nanoparticles deposited on nitrogen-doped mesoporous carbon gave 93% selectivity at complete conversion[25] and palladium nanoparticles supported on ZIF-8 were 90% selective for hydrocinnamaldehyde.[26]

Preliminary catalytic reactions were conducted in a stirred bench-top reactor using 0.5–1.0 mol% **1c** or **2c** and varying the temperature, pressure and solvent in order to identify an optimum system and conditions. Table 1 reveals that the solvent has quite a dramatic effect on both selectivity and conversion with **1c** and **2c** both giving high conversions and good selectivity in water and water/ethanol while reactions conducted in conventional organic solvents gave lower conversions and/or selectivities. The potential green benefits and practical advantages associated with aqueous phase catalysis promoted us to use this solvent for the remainder of our studies. For comparison, 1 mol% Pd/C catalysed this hydrogenation under the same conditions but only reached 60% conversion and 67% selectivity after 1 h at 60 °C.

Further optimisations explored the effect of temperature and pressure on performance. Interestingly, the selectivity for hydrocinnamaldehyde increased with temperature from 85% at 20 °C to 92% at 60 °C with 0.5 mol% PdNP@PPh_2-PEGPIILP under 70 psi of hydrogen in water; a similar improvement in selectivity was also obtained for PdNP@PPh_2-PIILP under the same conditions (Table S1, ESI‡). While these selectivities compare favourably with the vast majority of polymer and mesoporous carbon or silica-stabilised PdNP systems they fall short of the 96% obtained with AuPd-ordered mesoporous carbon. However, the overwhelming majority of these studies have been conducted in either isopropanol or a conventional organic solvent whereas PdNP@PPh_2-PEGPIILP has the distinct advantage of operating most efficiently in water.

Table 1 Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde as a function of catalyst, solvent and temperature[a]

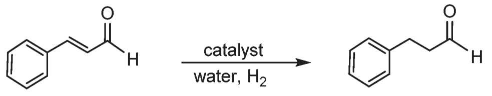


Catalyst	Solvent	Temp. (°C)	Conv.[b] (%)	TOF[c] (h^{-1})	Selectivity[b] (%)
1c	Toluene	25	0	0	0
2c	Toluene	25	23	46	78
1c	Ethanol	25	57	57	69
2c	Ethanol	25	54	108	76
1c	Hexane	25	35	35	58
2c	Hexane	25	52	104	82
1c	Ethyl acetate	25	10	10	58
2c	Ethyl acetate	25	29	58	85
1c	2-MeTHF	25	22	22	48
2c	2-MeTHF	25	35	70	62
1c	Water	25	75	75	74
2c	Water	25	81	162	85
1c	Water/ethanol[d]	25	82	82	72
2c	Water/ethanol[d]	25	75	150	74
Pd/C	Water[e]	60	60	60	67

[a] Reaction conditions: 1 mmol cinnamaldehyde, **1c** (1.0 mol%), **2c** (0.5 mol%), 10 mL solvent, 70 psi H_2, time = 1 h, temperature. [b] Yields and selectivities determined by ^{1}H NMR spectroscopy using 1,3-dinitrobenzene as an internal standard. Average of three runs. [c] Moles product per mole catalyst per hour based on the total palladium content. [d] 1/1 water/ethanol. [e] 1 mol% Pd/C, reaction run at 60 °C.

Interestingly, addition of a base to the catalytic reaction mixture resulted in a marked and substantial improvement in the selectivity for hydrocinnamaldehyde such that reactions catalysed by **2c** in the presence of either potassium carbonate, potassium phosphate or sodium hydroxide gave complete conversion with 100% selectivity for hydrocinnamaldehyde at room temperature in short reaction times (Table 2). This is the

Table 2 Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde as a function of base catalysed by PdNP@PPh_2-PIILP (**1c**) and PdNP@PPh_2-PEGPIILP (**2c**)[a]



Catalyst	Base	Conversion[b] (%)	TOF[c] (h^{-1})	Selectivity[b] (%)
1c	NaOH	27	27	90
2c	NaOH	>99	200	100
1c	K_2CO_3	43	43	95
2c	K_2CO_3	>99	200	100
Pd/C	K_2CO_3	42	44	93
1c	K_3PO_4	49	49	93
2c	K_3PO_4	100	200	100
1c	NEt_3	24	24	91
2c	NEt_3	90	180	88

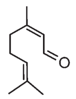
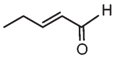
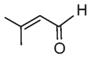
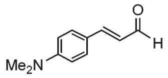
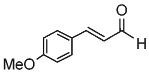
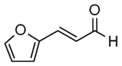
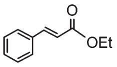
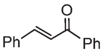
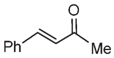
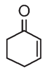
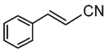
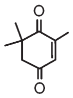
[a] Reaction conditions: 1.0 mmol cinnamaldehyde, 1.0 mmol base, **1c** (1.0 mol%), **2c** (0.5 mol%) or Pd/C (1.0 mol%), 12 mL water, 70 psi H_2, reaction time = 1 h, 25 °C. [b] Yields and selectivities determined by ^{1}H NMR spectroscopy using 1,3-dinitrobenzene as an internal standard. Average of three runs. [c] Moles product per mole catalyst per hour based on the total palladium content.

highest selectivity to be reported for the aqueous phase hydrogenation of cinnamaldehyde and even though near 100% selectivity has been obtained with Pd/C in ionic liquids, reactions were slower than in conventional solvents and the ionic liquid was extremely expensive.[27] A survey of the conversion as a function of the amount of base revealed that high activity and selectivity were retained even in the presence of as little as 10 mol% base. Although an increase in selectivity was also obtained for reactions catalysed by **1c** the conversion dropped quite significantly for each base tested, reinforcing the value of the PEGylated design feature.

A marked improvement in the activity and selectivity has previously been reported for the hydrogenation of cinnamaldehyde over CeO_2–ZrO_2-supported platinum in the presence of an added base; in this case the selectivity for cinnamyl alcohol increased from 60% to 97% while TOFs increased from 586 to 1233 h^{-1}.[28] A benchmark comparison with Pd/C achieved 93% selectivity for hydrocinnamaldehyde under the optimum conditions but a much lower conversion of 42%; although markedly less efficient than PdNP@PPh_2-PEGPIILP this represents a significant improvement on the 67% selectivity and 60% conversion obtained at 60 °C in the absence of a base (Table 1).

The optimum conditions identified above have also been applied to the hydrogenation of a selection of other α,β-unsaturated aldehydes including citral, *trans*-pentenal, 3-methylcrotonaldehyde 4-dimethylaminocinnamaldehyde, 4-methoxycinnamaldehyde and 3-(furan-2-yl)acrolein (Table 3).

Table 3 Selective hydrogenation of α,β-unsaturated aldehydes and ketones catalysed by PdNP@PPh_2-PEGPIILP (**2c**)

Substrate[a]			
Conversion[b] Selectivity[b]	99% (75 min) 100%[c]	98% (75 min) 100%	99% (75 min) 100%
Substrate[b]			
Conversion[b] Selectivity[b]	98% (75 min) 97%	99% (75 min) 98%	97% (75 min) 67%
Substrate[a]			
Conversion[b] Selectivity[b]	99% (360 min) 100%	98% (240 min) 100%	94% (240 min) 100%
Substrate[a]			
Conversion[b] Selectivity[b]	99% (120 min) 100%	96% (120 min) 100%	100% (240 min) 92%

[a] Reaction conditions: 1.0 mmol substrate, 1.0 mmol K_2CO_3, **2c** (0.5 mol%), 12 mL water, 70 psi H_2, reaction time given in parentheses after conversion (min), reaction temp = 25 °C. [b] Yields and selectivities determined by ^1H NMR spectroscopy using 1,3-dinitrobenzene as an internal standard. Average of three runs. [c] Selectivity of the α,β-unsaturated double bond.

The first three gave the saturated aldehyde as the sole product in excellent yield while 4-dimethylaminocinnamaldehyde and 4-methoxycinnamaldehyde gave high conversions with 98% and 99% selectivity for the corresponding hydrocinnamaldehyde. However, 3-(furan-2-yl)acrolein reached 97% conversion but only 67% selectivity for the desired saturated aldehyde with 3-tetrahydrofuran-2-yl-propionaldehyde as the only other significant product. In this regard, high selectivities for 3-(2-furyl)propanal have recently been reported with a RuNP catalyst stabilised by a poly(citric acid-β-cyclodextrin) polymer but in each case the conversion was very low (8–38%).[29] Similarly, ethyl cinnamate, benzylidene acetone, chalcone and cyclohexenone all gave the corresponding saturated ketone as the sole product in high yield (94–99%) albeit after longer reaction times of 2–4 h. The same protocol was successfully extended to cinnamonitrile to afford the corresponding saturated nitrile as the sole product in high yield after only 2 h at room temperature. Finally, ketoisophorone gave 2,6,6-trimethyl-1,4-cyclohexanedione (levodione) as the major product in 92% selectivity together with minor amounts of 4-hydroxy-3,3,5-trimethyl-cyclohexanone and 4-hydroxy-3,5,5-trimethyl-cyclohex-2-enone.

The effect of the base on selectivity was particularly dramatic for the hydrogenation of ketoisophorone as the selectivity dropped to 50% when the reaction was run under identical conditions in the absence of potassium carbonate. High selectivity for the C═C bond in ketoisophorone has previously been reported for alumina-supported platinum in the presence of tertiary amine bases whereas its palladium counterpart was more selective for reduction of the sterically hindered carbonyl group.[30] Gratifyingly, **2c** is also a highly efficacious catalyst for the aqueous phase reduction of aromatic nitro compounds giving the corresponding amines as the sole product in quantitative yields under mild conditions; further details will be disclosed in a subsequent report.

Reasoning that an aqueous phase compatible catalyst should lend itself to facile separation and recovery, recycle experiments were conducted on the hydrogenation of cinnamaldehyde with 0.5 mol% PdNP@PPh_2-PEGPIILP under optimum conditions by extracting the product and unreacted substrate and recharging the catalyst solution with cinnamaldehyde. The data in Fig. 4 are encouraging as the catalyst retained its high selectivity over the first five runs with only a minor drop in conversion; the latter is most likely due to catalyst attrition during the separation and catalyst recovery protocol rather than deactivation. To this end, ICP analysis of the aqueous phase collected after the fifth run revealed that the palladium content had decreased from 44 ppm (0.5 mol%) to 28 ppm; this corresponds to a 38% decrease in catalyst across five recycles which would account for the gradual decrease in conversion. TEM analysis of the catalyst solutions after the fifth run confirmed that the palladium nanoparticles in **2c** remained monodisperse with a mean diameter of 1.97 ± 0.38 nm (see the ESI for details‡).

Finally, we have recently begun to examine the influence on catalyst performance of each component and started by preparing PdNP@PPh_2PEGstyrene (**3c**) and PdNP@PEGPIILP (**4c**)

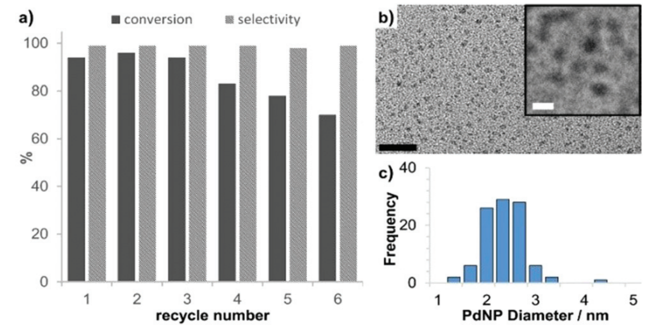
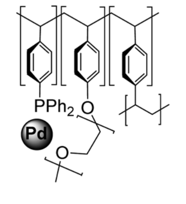
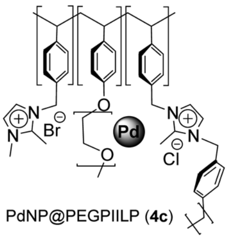


Fig. 4 (a) Recycling study for the hydrogenation of cinnamaldehyde in water catalysed by PdNP@PPh$_2$-PEGPIILP (**2c**) and (b) HRTEM images and (c) particle size distribution for PdNP@PPh$_2$-PEGPIILP (**2c**) after five recycles revealing an average NP size of 1.97 ± 0.38 nm. Scale bars are 25 nm (black) and 5 nm (white).

Table 4 Selective hydrogenation of cinnamaldehyde as a function of catalyst composition

Catalyst[a]	 PdNP@PPh$_2$PEGstyrene (**3c**)	 PdNP@PEGPIILP (**4c**)
Conversion[b]	72%	93%
TOF[c] (h^{-1})	144	132
Selectivity[b]	96%	82%

[a] Reaction conditions: 1.0 mmol substrate, 1.0 mmol K_2CO_3, **3c** (0.5 mol%) or **4c** (0.7 mol%), 12 mL water, 70 psi H_2, reaction time = 1 h, 25 °C. [b] Yields and selectivities determined by ^1H NMR spectroscopy using 1,3-dinitrobenzene as an internal standard. Average of three runs. [c] Moles product per mole catalyst per hour based on the total palladium content.

in order to systematically explore the effect of the immobilised ionic liquid and the PPh_2, respectively (Table 4). Although our initial study has been restricted to two modifications, removal of the imidazolium appears to reduce the activity while removal of phosphine reduces the selectivity. A series of additional modifications are currently underway to further elucidate the role of each component, full details of which will be reported in due course.

Conclusions

Phosphino-decorated polymer immobilised ionic liquid stabilised PdNPs are highly efficient catalysts for aqueous phase chemoselective hydrogenation of α,β-unsaturated aldehydes and ketones. Modification of the support with PEG improved catalyst performance such that near quantitative conversions and 100% selectivity for addition to the C=C double bond could be achieved under mild conditions and in short reaction times; these are the highest selectivities to be reported for the aqueous phase hydrogenation of this class of substrates. At this stage we do not have sufficient data to speculate about the mechanism of catalysis but *in situ* investigations on modified catalysts are now underway to explore the role of the phosphine, imidazolium and PEG. We are currently extending this family of catalysts to include a range of protic and aprotic heteroatom donors in order to explore their influence on the properties of the NP and their performance as catalysts, engineering a continuous flow process for aqueous phase chemoselective hydrogenation and developing a parallel approach based on tailor made heteroatom donor-modified mesoporous ionic liquid functionalised silica.

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