Highly Selective and Solvent-Dependent Reduction of Nitrobenzene to N-Phenylhydroxylamine, Azoxybenzene and Aniline Catalyzed by Phosphino-Modified Polymer Immobilized Ionic Liquid-Stabilized AuNPs

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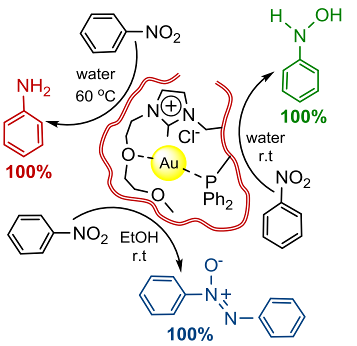

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ABSTRACT: Gold nanoparticles stabilized by phosphine-decorated polymer immobilized ionic liquids (AuNP@PPh$_2$-PIILP) is an extremely efficient multi-product selective catalyst for the sodium borohydride-mediated reduction of nitrobenzene giving either *N*-phenylhydroxylamine, azoxybenzene or aniline as the sole product under mild conditions and a very low catalyst loading. The use of a single nanoparticle-based catalyst for the partial and complete reduction of nitroarenes to afford three different products with exceptionally high selectivities is unprecedented. Under optimum conditions, thermodynamically unfavorable *N*-phenylhydroxylamine can be obtained as the sole product in near quantitative yield in water whereas a change in reaction solvent to ethanol results in a dramatic switch in selectivity to afford azoxybenzene. The key to obtaining such a high selectivity for *N*-phenylhydroxylamine is the use of a nitrogen atmosphere as reactions conducted under an inert atmosphere occur via the direct pathway and are essentially irreversible while reactions in air afford significant amounts of azoxy-based products by virtue of competing condensation due to reversible formation of *N*-phenylhydroxylamine. Ultimately, aniline can also be obtained quantitatively and selectively by adjusting the reaction temperature and time accordingly. Introduction of PEG onto to the polyionic liquid resulted in a dramatic improvement in catalyst efficiency such that *N*-phenylhydroxylamine could be obtained with a TON of 100,000 (TOF of 73,000 h^{-1}, with >99% selectivity), azoxybenzene with a TON of 55,000 (TOF of 37,000 h^{-1} with 100% selectivity) and aniline with a TON of 500,000 (TOF of 62,500 h^{-1}, with 100% selectivity). As the combination of ionic liquid and phosphine are required to achieve high activity and selectivity further studies are currently underway to explore whether interfacial electronic effects influence adsorption and thereby selectivity and whether channeling of the substrate by the electrostatic potential around the AuNPs is responsible for the high activity. This is the first report of a AuNP-based system that can selectively reduce nitroarenes to either of two synthetically important intermediates as well as aniline and, in this regard, is an exciting discovery that will form the basis to develop new catalyst technology for implementation in a continuous flow process for scale-up.

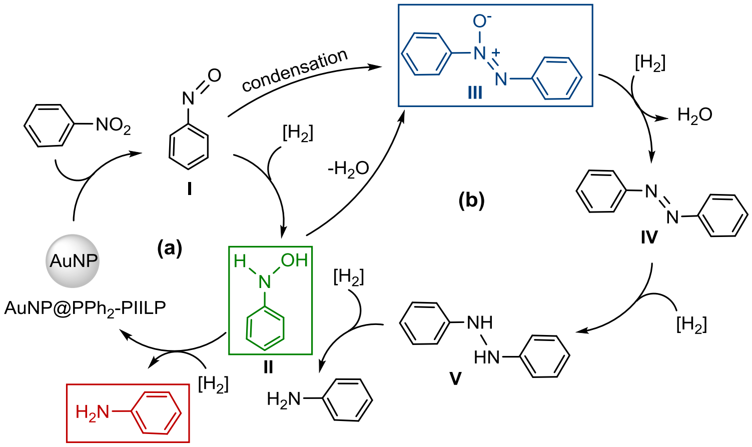
INTRODUCTION

Selectivity in catalysis is immensely important for the industrial scale production of commodity chemicals as well as fine chemicals and pharmaceuticals as it limits the production of waste, streamlines the process by avoiding or simplifying purification procedures, reduces costs and improves green credentials.[1] While selectivity in homogeneous catalysis is well-understood and can often be optimized by tuning steric and electronic parameters,[2] tuning selectivity of nanoparticles or heterogeneous catalysts is much more challenging and less-well developed.[3] To this end, until recently, the vast majority of studies have employed organic modifiers which improve or enhance selectivity through steric effects resulting from specific noncovalent molecular interactions.[4] However, there is now a growing body of evidence that activity and selectivity of nanoparticle-based catalysts can be modified/optimized by modulating their surface electronic structure. For example, PVP-stabilized rhodium nanoparticles modified with phosphine catalyze the chemoselective hydrogenation of functionalized aromatic compounds with >92% selectivity compared with 70% for the unmodified catalyst[5] while addition of tricyclohexylphosphine to silica-supported CuNPs results in a significant improvement for the semi-hydrogenation of 1-phenyl-1-propyne to *cis*-β-methylstyrene.[6] Other relevant studies include gold nanoparticles ligated by secondary phosphine oxides which catalyze the hydrogenation of α,β-unsaturated aldehydes with 100% selectivity for reduction of the carbonyl[7] and a pronounced ligand effect for RhNP and RuNP catalyzed hydrogenation of aromatic ketones[8] and substituted arenes.[9] Most recently, platinum nanoparticles stabilized on triphenylphosphine-modified silica showed markedly higher selectivity for the chemoselective hydrogenation of acetophenone and phenylacetylene than its unmodified counterpart; this too has been attributed to an increase in surface electron density by the electron donating phosphine.[10] In addition, amine-based modifiers have also been shown to alter the surface electronic structure of platinum nanowires and particles and thereby optimize reaction selectivity for the partial hydrogenation of nitroarenes to N-arylhydroxylamines.[11] The high activity of amino-modified Ru/γ-Al_2O_3 for the aqueous phase hydrogenation of levulinic acid to valerolactone was attributed to highly dispersed ruthenium centers with an electron-rich state[12] and the efficacy of RuNP stabilized in amine-modified porous organic polymers for the catalytic transfer hydrogenation of nitroarenes was attributed to a combination of nano-confinement and electron donation[13] while the efficacy of PdNPs supported on amine-rich silica hollow nanospheres for the hydrogenation of quinoline has been associated with an ultra-small particle size and high surface electron density.[14] Amine modified supports have been shown to improve activity and selectivity for PtNP, Pt/Co-NP and PdNP-catalyzed semi-hydrogenation of alkynes[15a-c] and selectivity for PtNP-catalyzed reduction of the C=O double bond in cinnamaldehyde[15d] while functionalization of platinum nanoparticles with *L*-proline enhances the activity and selectivity for the hydrogenation of acetophenone.[16] Aspartic acid also improves the activity and selectivity of platinum nanoparticle catalysts for the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols through cooperation of steric and electronic effects.[17] Finally, a series of elegant studies by the Glorious group have also demonstrated that the performance of supported heterogeneous catalysts can be tuned by surface modification with N-heterocyclic carbenes which activate unreactive Pd/Al_2O_3 for the Buchwald-Hartwig amination,[18] improve the selectivity of $Ru/K\text{-}Al_2O_3$ for the hydrogenation of aryl ketones and alkynes[19] and influence the performance and stability of ruthenium and palladium nanoparticles as catalysts for oxidations and reductions.[20]

We have recently been exploring the concept of HeteroAtom Donor-modified Polymer-Immobilized Ionic Liquid Stabilized NPs (NP@HAD-PIILS) reasoning that covalent attachment of an ionic liquid to a polymer would combine the favorable characteristics of ILs, such as their tunable physicochemical properties, ease of modification and enhancement in reaction rates and selectivity with the advantages associated with attachment to a solid support, to limit loss of ionic liquid, facilitate product separation, catalyst recovery and recycle and reduce the volume of IL as the catalyst is retained in a small amount of PIIL.[21] While heteroatom donors were initially incorporated into ionic liquids to stabilize NPs with respect to agglomeration under conditions of catalysis,[22] it is now clear that these donors could also enable the surface electronic structure to be modified and/or NP size and morphology to be controlled and, in this regard, HAD-PIILs may well prove to be tunable multifunctional supports for developing more efficient catalysts and processes.[14c,7a,15a,15d,22p] Gratifyingly, our initial foray in this area has proven extremely promising as PEG-modified phosphine-decorated polymer-immobilized ionic liquid-stabilized palladium nanoparticles were shown to be remarkably active and selective catalysts for hydrogenation of α,β-unsaturated aldehydes, ketones and nitriles, hydrogenation,[23] transfer hydrogenation of nitroarenes in water[24] and Suzuki-Miyaura cross-couplings in aqueous media.[25]

With the aim of further exploring the concept of PIIL stabilized NPs we have recently extended our study to include gold nanoparticle-based systems in order to undertake a comparative study of their efficacy as catalysts for the reduction of nitroarenes. Herein, we report that AuNP@PPh_2-

PIILP and its PEGylated counterpart AuNP@PPh$_2$-PEGPIILP are highly efficient and remarkably selective catalysts for the sodium borohydride-mediated reduction of nitroarenes to either *N*-phenylhydroxylamine, azoxybenzene or aniline (Scheme 1). Although AuNP catalyzed reduction of nitroarenes with sodium borohydride have been widely reported in the literature,[26] the overwhelming majority of systems are highly selective for aniline and this is the first example of a AuNP-based catalyst that is completely selective for reduction of nitroarenes to either *N*-arylhydroxylamine or the corresponding azoxyarene. Indeed, there are only two recent reports of selective hydrogenation of nitrobenzene to *N*-phenylhydroxylamine, one based on ethylenediamine-coated ultra-thin platinum nanowires[11a] the other platinum nanoparticles with an amine additive[11b] and both systems were based on hydrogenation rather than sodium borohydride-mediated reduction. Preliminary studies have also shown that both the phosphine and ionic liquid components are required to achieve high activity and selectivity, and that incorporation of PEG results in a significant improvement in catalyst efficacy.



Scheme 1 General mechanisms (Haber) for the reduction of nitroarenes (a) direct pathway (b) condensation pathway, highlighting the selective partial reduction to *N*-phenylhydroxylamine (green), azoxybenzene (blue) and complete reduction to aniline (red) achieved with AuNP@PPh$_2$-PIILP (**3a**) and AuNP@PPh$_2$-PEGPIILP (**3a.PEG**).

The selective partial hydrogenation of nitroarenes is of considerable interest as *N*-arylhydroxylamines are synthetically important intermediates to high value products including biologically active motifs,[27] polymerization inhibitors[28] and reagents for use in organic synthesis as they undergo a range of transformations including cyclizations,[29a] the Bamberger rearrangement[29b] and gold-catalyzed additions to multiple bonds.[29c] Although there are numerous procedures for the synthesis of *N*-arylhydroxylamines including stoichiometric reductions with zinc or tin[30] and catalytic reductions using hydrazine[31a-c] ammonia-borane[31d] or hydrogenation[11,32] most suffer severe limitations including low isolated yields, poor selectivity, slow rates, a lack of scalability and/or recyclability as well as poor environmental and economical credentials. Similarly, azoxyarenes are an important class of compound which find use as dyes, reducing agents and chemical stabilizers.[33] Azoxyarenes have been prepared by stoichiometric[34] or catalytic[33,35] oxidative coupling of arylamines as well as selective reduction of nitroarenes,[36] however, these approaches also suffer the same drawbacks as those detailed above for the selective synthesis of *N*-arylhydroxylamines. As such, the discovery of a single catalyst that is highly selective for the reduction of nitroarenes to *N*-arylhydroxylamines, azoxyarenes and the corresponding anilines at low catalyst loading in either water or ethanol under mild conditions is exceptional and will provide a platform to engineer new catalyst technology for efficient production of these target intermediates.

EXPERIMENTAL SECTION

Synthesis of Catalyst Precursor [$AuCl_4$]Cl@PPh_2-PIILP (2a). A round-bottomed flask was charged with PPh_2-PIILP (0.71 g, 0.79 mmol) and dichloromethane (25 mL). To this, was added $HAuCl_4$ (0.27 g, 0.79 mmol) in a single portion with rapid stirring. The resulting yellow solution was stirred at room temperature overnight under a nitrogen atmosphere. After this time, the solvent was removed *in vacuo* to yield a bright yellow powder which was washed with water (2 x 10 mL), ethanol (2 x 10 mL) and diethyl ether (2 x 10 mL) and dried under high vacuum to afford the desired precatalyst **2a** as a pale-yellow powder in 93% yield (0.9 g). ICP-OES data: 0.73 wt% gold and a gold loading of 0.037 mmol g^{-1}.

Synthesis of $[AuCl_4]Br@PPh_2$-PEGPIILP (2a.PEG). Tetrachloroaurate loaded polymer **2a.PEG** was prepared according to the procedure described above for **2a** and isolated as a pale-yellow powder in 87% yield. ICP-OES data: 3.1 wt% gold and a gold loading of 0.16 mmol g^{-1}.

General procedure for the selective reduction of nitroarenes to arylhydroxylamines. A Schlenk flask equipped with a magnetic stirrer was charged with precatalyst (0.5 μmol, 0.05 mol %) and evacuated and backfilled with nitrogen. $NaBH_4$ (0.096 g, 2.5 mmol) was added followed immediately by water (2.5 ml) and the resulting mixture stirred vigorously for 5 min at room temperature. After this time, nitroarene (1 mmol) was added and the reaction stirred for the appropriate time. The reaction was quenched by addition of water (5 mL), the product extracted with ethyl acetate (2 x 10 mL) and the solvent removed under reduced pressure. The residue was analyzed by ^1H NMR spectroscopy using 1,4-dioxane as internal standard to quantify the composition of starting material and products and determine the selectivity.

General procedure for the selective reduction of nitrobenzene to azoxybenzene. A Schlenk flash was charged with precatalyst (0.5 μmol, 0.05 mol % based on ICP) under a nitrogen atmosphere and $NaBH_4$ (0.096 g, 2.5 mmol) and ethanol (2 mL) added. The solution was stirred for 5 mins at room temperature after which time nitrobenzene (102 μL, 1 mmol) was added and the resulting mixture stirred for the appropriate time. The reaction was quenched by addition of water (5 mL) and the product extracted ethyl acetate (2 x 10 mL) and the solvent removed under reduced pressure. The residue was analyzed by ^{1}H NMR spectroscopy using 1,4-dioxane as internal standard to quantify the composition and selectivity.

General procedure for the reduction of nitroarenes to arylamines. A Schlenk flask was charged with precatalyst (0.5 μmol, 0.05 mol % based on ICP) under a nitrogen atmosphere and $NaBH_4$ (0.192 g, 5.0 mmol) and water (2 mL) added. The solution was then stirred for 5 mins at room temperature after which nitrobenzene (102 μL, 1 mmol) was added dropwise and the mixture heated to 60°C with stirring for the appropriate time. After this time, the reaction was cooled to room temperature then quenched with water (5 mL) the product extracted with ethyl acetate (2 x 10 mL) and the solvent removed under reduced pressure. The residue was analyzed by ^{1}H NMR spectroscopy using 1,4-dioxane as internal standard to quantify the composition and selectivity.

RESULTS AND DISCUSSION

Synthesis and characterization of phosphine-modified gold precatalysts and nanoparticles

The polymers, their tetrachloroaurate loaded precursors, and the corresponding polymer immobilized ionic liquid stabilized AuNPs developed in this project are shown in Figure 1. Polymer immobilized ionic liquids **1a** and **1b** were prepared by AIBN-initiated radical polymerization of the constituent imidazolium-modified monomer or its PEGylated counterpart with cation appropriate cross-linker and 4-diphenylphosphinostyrene in the desired ratio. Both polymers were impregnated by exchanging half of the halide anions with $[AuCl_4]^-$ to afford the corresponding tetrachloroaurate-loaded precursors **2a** ($[AuCl_4]Cl@PPh_2$-PIILP) and **2a.PEG** ($[AuCl_4]Br@PPh_2$-PEGPIILP) which have a gold to phosphine stoichiometry of one; full characterization details are provided in the ESI. As we have previously demonstrated that palladium nanoparticle-based catalysts generated *in situ* by reduction of the corresponding tetrachloropalladate-loaded precursor immediately prior to use are as efficient as their *ex situ* prepared counterparts, precursors **2a** and **2a.PEG** were used for catalyst evaluation and optimization while samples of **3a** and **3a.PEG** were generated under conditions of catalysis to obtain TEM and XPS characterization data on the active species. The generation of catalyst *in situ* immediately prior to addition of substrate offers a number of potential practical advantages as it eliminates the need to prepare, isolate and store nanoparticle catalysts, and as such streamlines the protocol; it also improves versatility by enabling different reducing agents and/or conditions to be examined and thereby facilitates rapid catalyst and reaction screening.

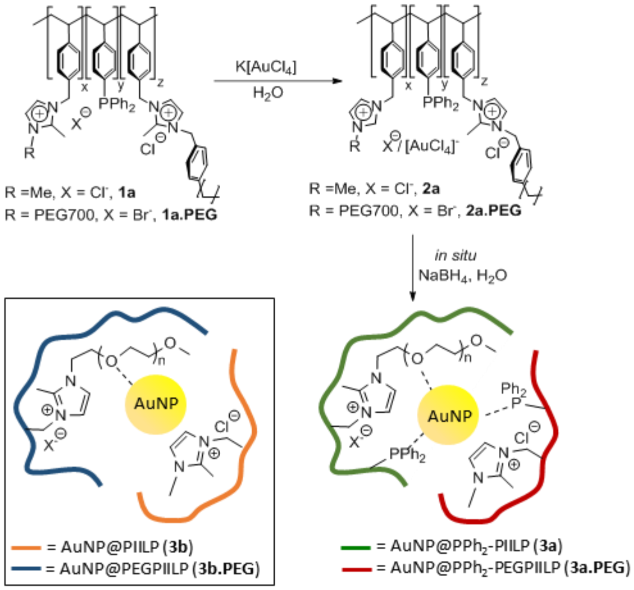


Figure 1 Composition of polymers **1a** and **1a.PEG**, synthesis of $[AuCl_4]^-$ impregnated polymers **2a** and **2a.PEG** and PIILP-stabilized gold nanoparticles **3a** (red) and **3a.PEG** (green) and composition of **3b** (orange) and **3b.PEG** (blue).

The gold loadings of precatalysts **2a** and **2a.PEG** were determined to be 0.037 mmol g^{-1} and 0.16 mmol g^{-1}, respectively, using ICP-OES. The solid state ^{31}P NMR spectra of **2a** and **2a.PEG** confirm the presence of a Au----P interaction which is clearly evident from the low field chemical shifts of δ 27.1 and 24.5 ppm, respectively; for comparison the ^{31}P NMR signals for polymers **1a** and **1a.PEG** appear at δ -5 and -10.4 ppm, respectively; these complexation shifts[37] are similar to previously reported values.[38] The ^{13}C CP/MAS NMR spectra of **1a** and **1a.PEG** and **2a** and **2a.PEG** contain a set of characteristic signals between δ 124-144 ppm associated with the imidazolium ring and the aromatic carbon atoms as well as signals in the range δ 11-50 ppm which correspond to the methyl groups attached to the imidazolium ring and the aliphatic carbon atoms of the polystyrene backbone. ATR-IR spectra of catalysts **2a** and **2b**, treated *in-situ* with $NaBH_4$/ethanol solution to form AuNP, showed no adsorption of CO due to weak adsorption of CO on metallic Au. Surface characterization of the tetrachloroaurate-loaded precursors (**2a, 2b, 2a.PEG** and **2b.PEG**) and equivalent reduced catalysts (**3a, 3b, 3a.PEG** and **3b.PEG**) was undertaken by X-ray photoelectron spectroscopy (XPS) and a shift in the Au $4f_{5/2}$ and Au $4_{7/2}$ doublets to lower binding energies upon reduction was observed (see ESI file for details). For example, Au $4_{7/2}$ binding energies of 87.4 eV for **2b** and 87.6 eV for **2b.PEG** are entirely consistent with the Au^{3+} ion[39a,b] whilst 83.8 eV for **3b** and 83.8 eV for **3b.PEG** are assigned to a lower oxidation state of the Au species (Au^0) (Figure 2a-b).[39b,c] The presence of additional Au $4f_{5/2}$ and Au $4f_{7/2}$ doublets in the precursor spectra at higher binding energies than the Au^0 doublets of the chemically reduced catalysts are assigned as Au^1 species resulting from decomposition caused by exposure to the X-ray source during acquisition,[39d] this is particularly evident in the spectra for **2a** in which the sample has undergone near complete reduction. This is verified by considering the N 1s region, which along with the expected signal for the imidazolium environment in each sample, shows additional signals at lower binding energies corresponding to uncharged, and in some cases anionic, nitrogen species which are assigned to damage.[39e] There is no evidence from the XPS of any Au---P interactions caused by electron donation from the phosphino group, identified by solid state NMR spectroscopy as the binding energies for the Au 4f$_{5/2}$ and Au 4f$_{7/2}$ doublets for both **2a** and **2a.PEG** are very similar to those of **2b** and **2b.PEG** (Figure 2b and ESI); moreover, no shift in the BEs of the P 2p$_{3/2}$ and P 2p$_{1/2}$ doublets was observed upon reduction of the gold salt (Figure 2c).

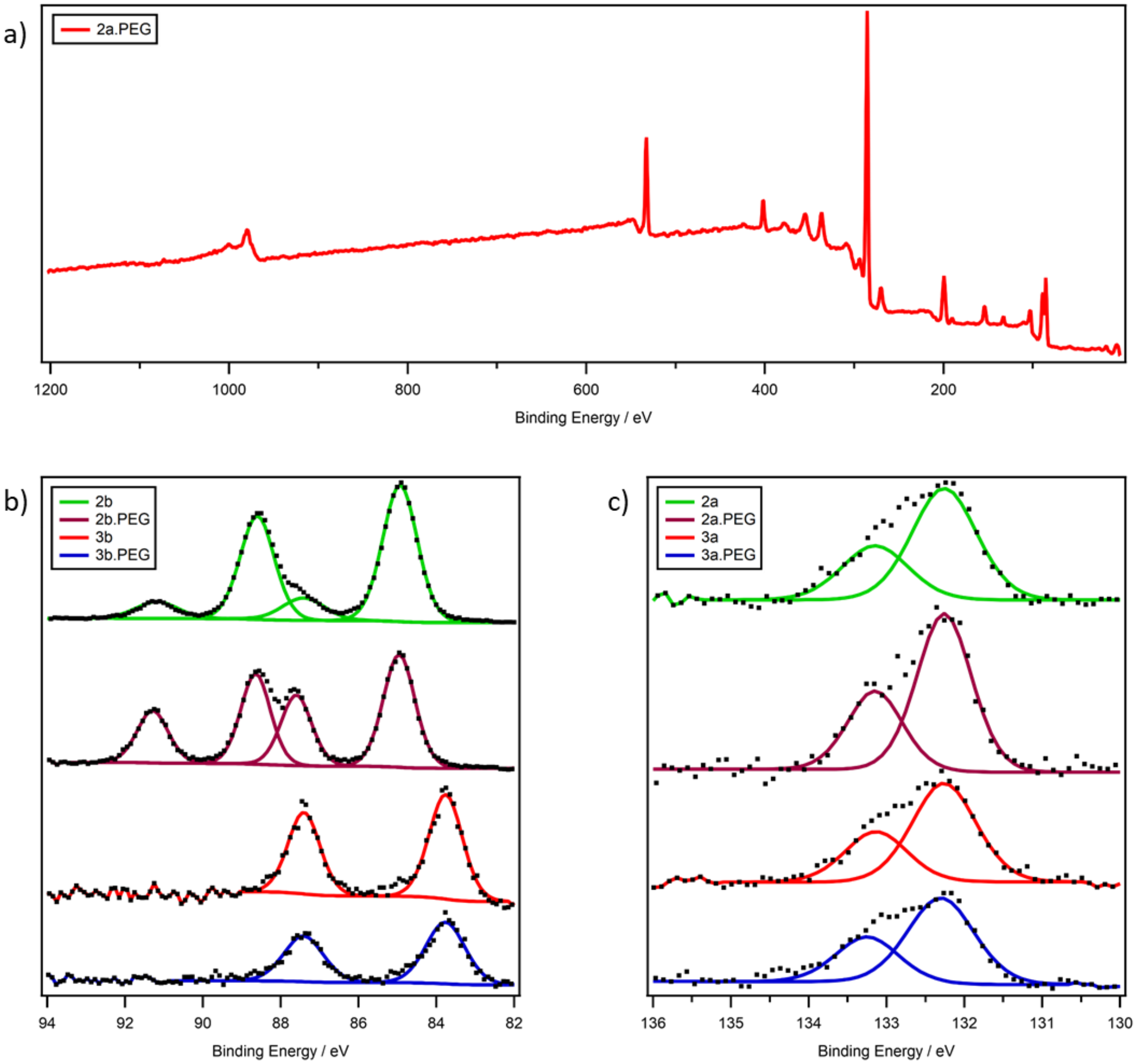


Figure 2 XPS scan showing a) full scan of **2a.PEG**; b) Au 4f core level of **2b, 2b.PEG** and **3b** and **3b.PEG**; and (c) P 2p core level of **2a**, **2a.PEG** and **3a** and **3a.PEG**. All referenced to the C 1s alkyl peak at 284.8 eV.

TEM micrographs of *in situ* generated **3a** and **3a.PEG** revealed that the gold nanoparticles were near monodisperse with average diameters of 3.4 ± 0.9 and 2.5 ± 0.6 nm, respectively, representative micrographs and associated distribution histograms based on > 100 particles are shown in Figure 3. Interestingly, we have recently reported that palladium nanoparticles stabilized by PPh_2-PIILP and PPh_2-PEGPIILP have vastly disparate sizes and those stabilized by polymer immobilized ionic liquid containing PEG and PPh_2 were also smaller than those stabilized by PPh_2-modifed PIIL; thus, the number and type of heteroatom donor may well influence nucleation and growth of NPs. The strong surface plasmon resonance (SPR) adsorption for AuNPs is dependent on the size and shape as well as the dielectric constant of the local medium which for this study will be associated with the nature of the polymeric shell.[40,41] The strong SPR bands at 519 nm in the UV-vis spectra of AuNP@PPh_2-PIILP (**3a)** and AuNP@PPh_2-PEGPIILP **(3a.PEG)** and at 517 nm for AuNP@PEG-PIILP (**3b.PEG**) are consistent with formation of spherical particles while λ_{max} for AuNP@PIILP (**3b**) is red shifted to 525 nm, which may well reflect the different nature of the ligand-surface interactions stabilizing the NPs as the ionic microenvironment in each is approximately the same but **3b** is the only system that does not contain heteroatom donor atoms. As a comparison, gold nanoparticles stabilized by neutral PEG-modified heteroatom donor mono-bis- and tris-1,2,3-triazoles as well as nona-PEG-branched triazole dendrimers with diameters close to 3 nm also exhibit SPR bands around 515 nm.[26e-g]

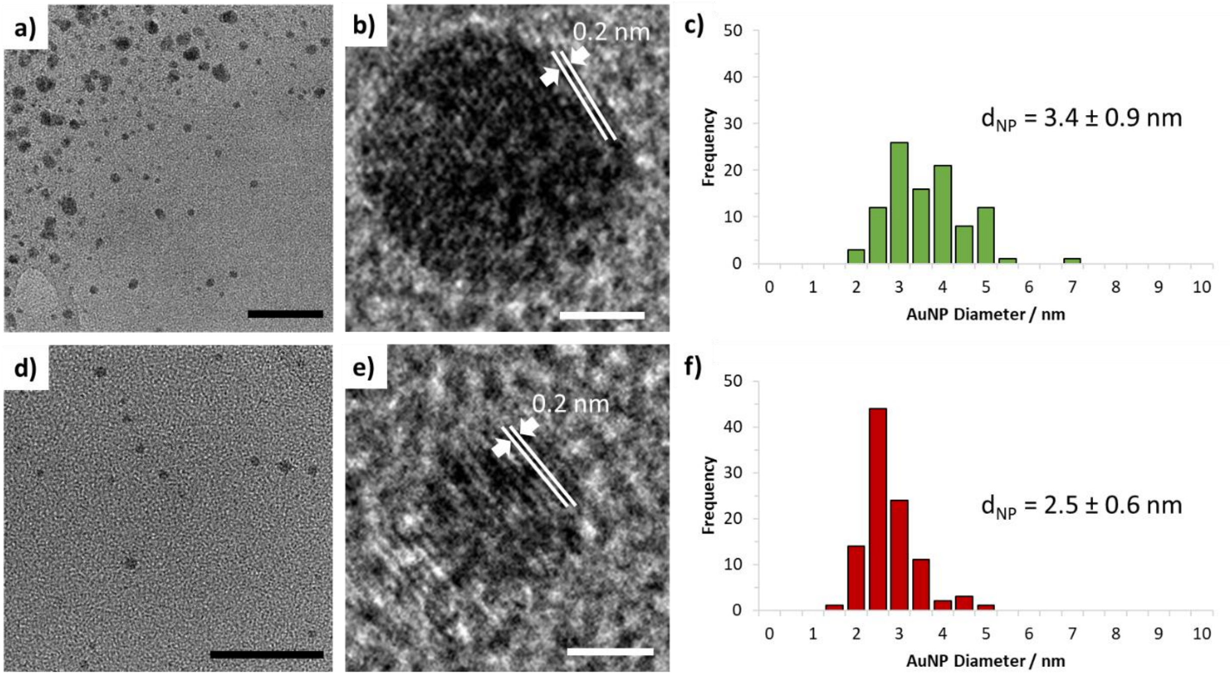


Figure 3 HRTEM images of (a-b) **3a** and (d-e) **3a-PEG**, with the observed atomic spacing (parallel white lines) confirming the metallic nature of the AuNPs, and (c and f) corresponding particle size distributions determined by counting >100 particles. Mean nanoparticle diameters are of 3.4 ± 0.9 and 2.5 ± 0.6 nm, nm for **3a** and **3a-PEG**, respectively. Black and white scale bars are 25 and 1 nm, respectively.

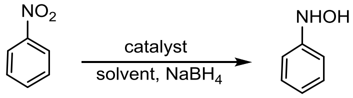
Selective Reduction of Nitrobenzene to *N*-Phenylhydroxylamine

The reduction of nitroarenes was initially targeted on the basis that there have been two recent reports that nitrogen donor-modified platinum nanoparticles selectively catalyze the highly selective partial hydrogenation of nitrobenzene to *N*-phenylhydroxylamine.[11] As the high selectivity of these systems was attributed to electron donation from the amine to the surface platinum atoms we became interested in exploring and comparing the efficacy of phosphine decorated PIIL stabilized AuNPs as catalysts for the reduction of nitroarenes to assess the influence of the heteroatom donor on selectivity. To this end, we have recently demonstrated that PdNP@PIILP are highly efficient catalysts for the complete reduction of nitroarenes to the corresponding aniline in water under extremely mild conditions and the TOF of 17,125 h^{-1} is the highest to be reported for the aqueous phase transfer hydrogenation of a nitroarene catalyzed by a PdNP-based system.[24]

A series of catalytic reactions were initially conducted with nitrobenzene as the benchmark substrate using a protocol recently developed for the PdNP-catalyzed reduction of nitroarenes as a lead.[24] A preliminary reaction conducted in water under air for 2 h at 25 °C using a 0.005 mol% loading of AuNP@PPh_2-PIILP (**3a**), generated *in situ* by reduction of tetrachloroaurate loaded **2a**, with a substrate:$NaBH_4$ ratio of 2.5 gave 35% conversion and 62% selectivity for *N*-phenylhydroxylamine (Table 1 entry 1). Under these conditions azoxybenzene was identified as the other major species (10%) together with trace amounts of azobenzene (2%) and aniline (2%). Speculating that reversible reduction of rapidly formed nitrosobenzene to *N*-phenylhydroxylamine in air would facilitate access to the condensation pathway to afford azoxy-based reduction products, the same reaction was conducted under a nitrogen atmosphere. Gratifyingly, under otherwise identical conditions, reaction under a nitrogen atmosphere resulted in a dramatic improvement in selectivity from 62% to 97% as well as an increase in conversion to 45%; moreover, high selectivity for *N*-phenylhydroxylamine was retained at full conversion when the reaction time was extended to 2 h (Table 1 entry 2-3). Thus, it appears that irreversible formation of *N*-phenylhydroxylamine under nitrogen suppresses the condensation pathway as only trace quantities of azoxybenzene (1%) and aniline (<1%) were detected by NMR spectroscopy and GLC analyses. Indeed, we are confident that azoxybenzene only forms after exposure of the sample to oxygen during work-up, as monitoring of the NMR sample showed a significant increase in azoxybenzene with time at the expense of *N*-phenylhydroxylamine; as such all subsequent studies were conducted with careful and meticulous exclusion of air. A survey of the performance of **3a** in selected solvents revealed that the highest conversions and selectivities were obtained in water whereas markedly lower yields and/or selectivities were obtained under the same conditions in ethanol, a 1:1 mixture of ethanol and water, 2-methyltetrahydrofuran, a 1:1 mixture of water and 2-methyltetrahydrofuran and toluene (Table 1 entries 2-8). Most interestingly, this study revealed that the use of ethanol as solvent gave a complete switch in selectivity to afford azoxybenzene as the sole product albeit with a conversion of only 32% (v*ide infra*). Thus, water was identified as the solvent of choice based on the high conversion and superior and unprecedented selectivity for *N*-phenylhydroxylamine as well as its environmentally benign properties, practical advantages and the potential benefit of the hydrophobic effect.

Variation of the catalyst loading revealed that the optimum combination of conversion and selectivity was obtained with 0.005 mol% **3a** as a loading of 0.025 mol% resulted in a slight drop in selectivity due to formation of aniline (Table 1 entry 9). As a large excess of sodium borohydride is often employed for the reduction of nitroarenes, the $NaBH_4$:substrate ratio was varied and conversions were shown to increase quite dramatically from 9% with 1.0 equivalent eventually reaching a plateau of 71% with 15 equivalents (Figure 4). While this profile is a clear indication of mass transfer limited availability of reducing agent, the TOFs will still be limited by the poor solubility of the substrate in water even with an excess of borohydride. As such, all further studies were conducted using 2.5 equivalents of $NaBH_4$ as this was considered to be the best compromise giving good conversions after a relatively short reaction time (2 h); the use of only a slight excess of reducing agent also improves the overall atom efficiency.

Table 1 Selective reduction of nitrobenzene to *N*-phenylhydroxylamine by $NaBH_4$ as a function of catalyst, solvent and temperature.[a]



entry	Catalyst	Solvent	Temp (°C)	Mol% cat	Time (min)	Conv (%)[b]	Select (%)[c]
1	**3a**[d]	water	25	0.005	40	35	62
2	**3a**[e]	water	25	0.005	40	45	97
3	**3a**[e]	water	25	0.005	120	100	96
4	**3a**[e]	EtOH	25	0.005	40	19	0
5	**3a**[e]	EtOH/water	25	0.005	40	34	92
6	**3a**[e]	2-MeTHF	25	0.005	40	1	>99
7	**3a**[e]	2-THF/water	25	0.005	40	17	98
8	**3a**[e]	toluene	25	0.005	40	2	>99
9	**3a**[e]	water	25	0.025	40	81	92
10	**3a**[e]	water	50	0.005	40	100	83
11	**3a.PEG**[e]	water	25	0.005	40	100	>99
12	**AuNP@citrate**[e]	water	25	0.005	40	21	83
13	**3b**[e]	water	25	0.005	40	27	97
14	**3b.PEG**[e]	water	25	0.005	40	55	96

[a] Reaction conditions: 1 mmol nitrobenzene, mol% Au in **3a**, **3a.PEG, 3b**, **3b.PEG** and AuNP@citrate, 2 mL solvent, 2.5 mmol $NaBH_4$, time, temperature. [b] Yields determined by ^1H NMR spectroscopy using dioxane as internal standard and gas chromatography using decane as internal standard. Average of at least three runs. [c] Selectivity for *N*-phenylhydroxylamine [%*N*-phenylhydroxylamine / (%*N*-phenylhydroxylamine + % azoxybenzene + % azobenzene + % aniline)]/ x 100%. [d] reaction conducted in air. [e] Reaction conducted under N_2.

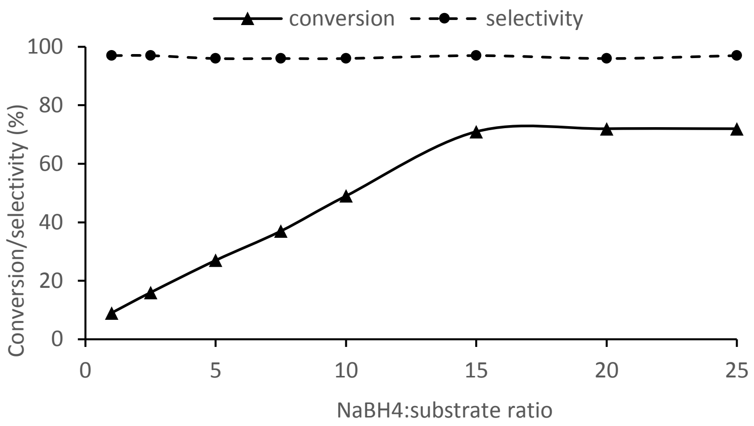


Figure 4 Reaction profile as a function of the $NaBH_4$:substrate ratio for the reduction of nitrobenzene in water at 25 °C catalyzed by 0.005 mol% **3a** for a reaction time of 30 min.

Selectivity for *N*-phenylhydroxylamine decreased with an increase in the reaction temperature due to the formation of increasing amounts of aniline; for example, *N*-phenylhydroxylamine and aniline were obtained in 83% and 14% yield, respectively, together with 3% azoxybenzene after 2 h at 50 °C (Table 1 entry 10). The nature of this temperature-dependent selectivity suggests that the activation barrier for reduction of *N*-phenylhydroxylamine to aniline with catalyst **3a** is significantly higher than that for reduction of nitrobenzene (or nitrosobenzene) to *N*-phenylhydroxylamine which allows high selectivities to be obtained for reactions conducted at lower temperatures. However, even though the activation barrier for reduction of *N*-phenylhydroxylamine to aniline is clearly high enough to obtain *N*-phenylhydroxylamine with high selectivity (96% at complete conversion after 2 h a 25 °C) it is also possible to obtain aniline as the sole product by increasing the reaction time and/or temperature accordingly (*vide infra*). Further kinetic studies will be required to elucidate the relative rate of *N*-phenylhydroxylamine formation compared with *N*-phenylhydroxylamine reduction. A control reaction for the reduction of nitrobenzene conducted at room temperature in water under nitrogen using 2.5 equivalents of $NaBH_4$ but in the absence of **3a** gave no conversions even after 3 h.

As the high selectivity of **3a** for *N*-phenylhydroxylamine was obtained in water the influence of introducing PEG on to the polymer immobilized ionic liquid was examined reasoning that an increase in hydrophilicity would improve water solubility and/or catalyst dispersibility and thereby efficiency while additional interactions between the oxygen donors of the ether and surface atoms of the nanoparticle could provide further stabilization. Under the same conditions identified above, 0.005 mol% **3a**.**PEG** catalyzed the reduction of nitrobenzene to give complete conversion with 99% selectivity for *N*-phenylhydroxylamine after a reaction time of only 40 min (Table 1 entry 11); this is a significant improvement on the efficacy of **3a** which required 2 h to reach 100% conversion (Table 1 entry 3). A comparative study of the variation in composition as a function of time for the reduction of nitrobenzene catalyzed by **3a** and **3a**.**PEG** at 25 °C (Figure 5) clearly shows the disparate rates of formation of *N*-phenylhydroxylamine which we tentatively attribute to the hydrophilicity of the PEGylated support facilitating access of the substrate to the active site. While AuNPs stabilized by an amphiphilic PEG-modified tris-triazole has recently been reported to be a highly active catalyst for the sodium borohydride-mediated reduction of 4-nitrophenol, in stark contrast to **3a.PEG** this system gave complete reduction to 4-aminophenol.[26z] The high selectivity of **3a-PEG** as a catalyst for the reduction of nitrobenzene to *N*-phenylhydroxylamine is clearly evident from a comparison of the ^1H NMR spectrum of a typical reaction mixture obtained after only 30 min (Figure 6b) with that of nitrobenzene (Figure 6a). As there are no reports of selective partial reduction of nitroarenes with gold-based nanoparticles, benchmark comparative catalyst testing was undertaken using a 0.005 mol% loading of AuNP@citrate generated *in situ* by reduction of potassium tetrachloroaurate with sodium citrate.[41] A comparison of the corresponding composition–time profile with AuNP@citrate under otherwise identical conditions further emphasizes the efficacy of **3a** and **3a-PEG** as a conversion of only 21% was obtained after 40 min (Table 1 entry 12); the lower selectivity of 83% was due to formation of azoxybenzene (2%) and aniline (2%). The low activity of AuNP@citrate is entirely consistent with recent work from the Astruc group as citrate-stabilized AuNPs were shown to be much less active than those stabilized by mono, bifunctional, polymeric and dendritic 1,2,3-triazoles terminated with PEG;[26e,g] the efficacy of these triazole-stabilized systems was attributed to weak coordination of the heteroatom donor to the nanoparticle surface and facile substitution by substrate.

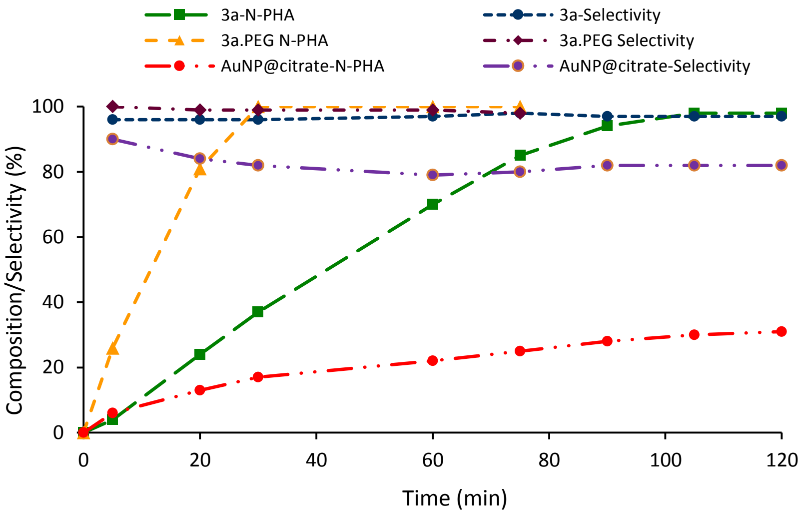


Figure 5 Reaction profile as a function of time for the selective partial reduction of nitrobenzene to *N*-phenylhydroxylamine (N-PHA) in water at 25 °C using 2.5 equivalents of $NaBH_4$ catalyzed by 0.005 mol% **3a**, **3a**.**PEG** or AuNP@citrate.

Finally, TEM analysis of the aqueous phase remaining after sodium borohydride-mediated reduction of nitrobenzene catalyzed by 0.005 mol% **3a.PEG** revealed that while the gold nanoparticles remained near monodisperse there was a slight increase in size with a mean diameter of 3.3 ± 1.1 nm compared to a sample examined before catalysis which had a mean diameter of 2.5 ± 0.6 nm; the micrograph and associated distribution histograms based on >100 particles is shown in the ESI (Figure S43).

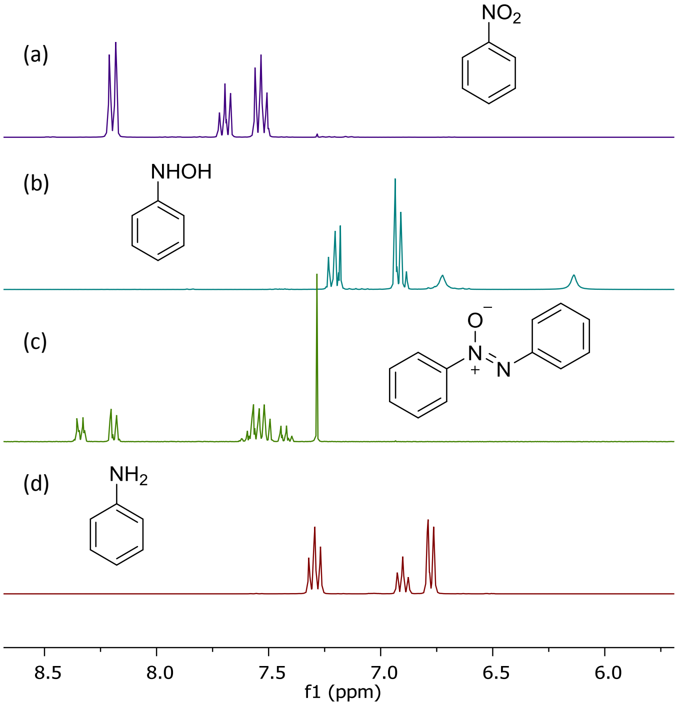


Figure 6 ^{1}H NMR spectra for the selective reduction of nitrobenzene catalyzed by **3a.PEG** (a) nitrobenzene, (b) *N*-phenylhydroxylamine (0.005 mol% **3a.PEG**, 25 °C, 30 min, 2.5 equiv. $NaBH_4$, water), (c) azoxybenzene (0.005 mol% **3a.PEG**, 25 °C, 2.5 h, 2.5 equiv. $NaBH_4$, ethanol) and (d) aniline (0.005 mol% **3a.PEG**, 50 °C, 6 h, 5.0 equiv. $NaBH_4$, water).

The influence of the diphenylphosphine and PEG components on catalyst performance has also been explored by comparing the performance of **3a** and **3a-PEG** against AuNP@PIILP (**3b**) and AuNP@PEG-PIILP (**3b.PEG**) which correspond to selective removal of the diphenylphosphino group from both. Under the same conditions a 0.005 mol% loading of **3b** gave 27% conversion and 97% selectivity for *N*-phenylhydroxylamine while the same loading of **3b.PEG** gave 55% conversion and 96% selectivity; thus selective removal of the diphenylphosphino group results in a significant drop in activity (Table 1 entries 13-14). In addition, the selective removal of the PEG results in a marked drop in activity as evidence by the conversions of 43% and 99% obtained with **3a** and **3a.PEG**, respectively, and 27% and 55% with **3b** and **3b.PEG**, respectively. While this may reflect an improvement in dispersibility for the PEG-based systems in water as the mean diameters of the nanoparticles in **3b** and **3b.PEG** are essentially the same (3.4 ± 1.1 and 3.3 ± 0.9 nm, respectively) it is interesting to note that the nanoparticles in the most efficient catalyst (**3a.PEG**) are significantly smaller (2.5 ± 0.6 nm) than each of the other systems examined and as such further catalyst modifications and associated studies will be required to deconvolute what factors control or influence catalyst performance.

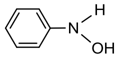
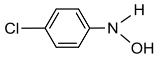
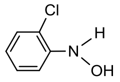
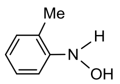
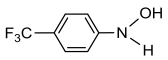
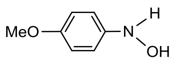
The efficacy of **3a.PEG** was further tested by reducing the catalyst loading to 0.0002 mol% and under otherwise identical conditions the conversion of 22% to *N*-phenylhydroxylamine with 100% selectivity after only 1.5 h corresponds to a turnover number (TON, measured as total moles of product per mole of catalyst) of 110,000 and a TOF of 73,000 h^{-1}. As this reaction is likely to be mass transfer limited due to poor solubility of the substrate, these turnover numbers are probably more representative of the potential intrinsic turnover rate of the catalyst, particularly as a further decrease in catalyst loading to 0.0001 mol% resulted in a marginal increase in TON to 112,000, in the same time. While there are a plethora of AuNP-based systems that catalyze the sodium borohydride-mediated reduction of nitroarenes,[26] the vast majority give complete reduction to the aniline and there are no reports of selective reduction to the corresponding *N*-arylhydroxylamine. Moreover, even though there are a few reports of catalysts that are selective for transfer hydrogenation of nitroarenes to *N*-arylhydroxylamines, including Rh/C with hydrazine,[31a]

Au/TiO_2 with NH_3BH_3,[43] Ag/TiO_2 with NH_3BH_3,[31d] Ru/polystyrene[44a] or RuNP/carbon nanotubes[44b] with hydrazine and Amberlite supported-PtNPs with hydrazine,[45] these systems suffer severe limitations such as the need for a high catalyst loading, high reaction temperatures and/or long reaction times, the use of organic solvents and/or low selectivities. The high selectivity and TOF obtained with **3a**.**PEG** in water under mild conditions at low catalyst loadings is unprecedented for a gold catalyst and the highest to be reported for the transfer hydrogenation of this class of substrate, which is quite remarkable given the challenging nature of the transformation; future studies will be directed towards understanding the origin of this efficacy. Moreover, the efficacy of **3a**.**PEG** even matches that of recently reported platinum-based systems that are highly selective for the hydrogenation of nitroarenes to N-arylhydroxylamines; both systems required surface modification with an amine-based donor to achieve high selectivity. In one case, the effect was attributed to an interfacial electronic effect which favors adsorption of the reactant over the electron rich *N*-phenylhydroxylamine while the other associated the selectivity to competitive adsorption; in this regard, future studies will further explore the influence of the phosphine donor on catalyst efficacy.

The protocol developed above has been applied to the aqueous phase reduction of selected nitroarenes to assess the potential scope and efficacy of **3a**.**PEG**. All reactions were conducted in water and the times varied to obtain the best compromise between yield and selectivity; full details are presented in Table 2. Good conversions were obtained for 2-chloro- and 4-chloronitrobenzene which gave the corresponding *N*-(2-chlorophenyl)- and *N*-(4-chlorophenyl)hydroxylamine in 95% and 93% selectivity, respectively. Interestingly, in contrast to many palladium-based systems, there was no evidence for competing hydrodehalogenation to afford either nitrobenzene or aniline.[46] An excellent conversion and high selectivity was also obtained with 4-

trifluoromethylnitrobenzene which gave *N*-(4-(trifluoromethyl)phenyl)hydroxylamine as the major product in 97% selectivity at 99% conversion, together with less than 3% of the corresponding aniline as the only other identifiably product. Similarly, under the same conditions *N*-(*o*-tolyl)hydroxylamine was reduced to the corresponding hydroxylamine *N-(o-*tolyl)hydroxylamine in 97% selectivity at 99% conversion. However, when the same protocol was applied to the reduction of 1-methoxy-4-nitrobenzene, as a representative example of a nitrobenzene substituted with an electron donating group, the reaction reached 79% conversion after 2h and 68% selectivity for the desired *N*-(4-methoxyphenyl)hydroxylamine with 4-methoxyaniline as the only other significant by-product.

Table 2 Partial reduction of nitroarenes to *N*-arylhydroxylamines with $NaBH_4$ catalyzed by AuNP@PPh_2-PEGPIILP (**3a.PEG**).[a]

Product			
Conversion[b]	>99% (1)[c]	80% (3)[c]	98% (1)[c]
Selectivity[b]	100%	93%	95%
Product			
Conversion[b]	99% (1)[c]	99% (1)[c]	79% (3)[c]
Selectivity[b]	97%	97%	68%

[a] Reaction conditions: 1 mmol substrate, 0.005 mol% **3a.PEG**, 2.0 mL water, 2.5 mmol $NaBH_4$, 25 °C, 2h. [b] Yields and selectivities determined either by ^1H NMR spectroscopy using dioxane as internal standard. Average of three runs [c] Average deviations (*d*) = $(|x_1 - \overline{x}| + |x_2 - \overline{x}| + |x_3 + \overline{x}|)/3$ where $\overline{x} = (x_1 + x_2 + x_3)/3$ and x_n is the conversion for run n. [d] *N*-arylhydroxylamine selectivity = [% *N*-arylhydroxylamine/(% *N*-arylhydroxylamine + % aniline + % azoxyarene)] x 100%.

Selective Reduction of Nitrobenzene to Azoxybenzene and Aniline

The dramatic solvent dependent selectivity for the reduction of nitrobenzene in water and ethanol identified in our preliminary optimization above prompted us to undertake a solvent screen by varying the ethanol-water ratio to identify the composition range that affords azoxybenzene in high selectivity. As the reduction of nitrobenzene in ethanol only reached 19% conversion after 40 min using 0.005 mol% **3a**, albeit with 100% selectivity for azoxybenzene, we chose to use **3a**.**PEG** for the solvent screen as it was markedly more active for the selective reduction of nitrobenzene to *N*-phenylhydroxylamine. High selectivity for *N*-phenylhydroxylamine was retained in water/ethanol mixtures even up to an ethanol content of 99% and the switch in selectivity only occurred in dry ethanol, with 0.005 mol% **3a.PEG** giving complete conversion to afford azoxybenzene as the sole product after 2.5 h at 25 °C. Moreover, aqueous workup of this reaction mixture resulted in the appearance of a significant amount of *N*-phenylhydroxylamine, suggesting that formation of azoxybenzene is reversible in the presence of reducing agent; this was confirmed by stirring an ethanol/water solution of commercially available azoxybenzene in the presence of 0.005 mol% **3a.PEG** and 2.5 equivalents of sodium borohydride in air for 15 min and comparing the ^{1}H NMR spectrum of the resulting mixture with those of authentic samples. Interestingly, *N*-phenylhydroxylamine was the only product detected under these conditions which may well be due to rapid reduction of the nitrosobenzene by-product that would be generated in the hydrolysis of azoxybenzene. The efficacy of **3a-PEG** as a catalyst for the selective reduction of nitrobenzene to azoxybenzene is evident from the ^{1}H NMR spectrum of the reaction mixture which shows complete consumption of substrate with azoxybenzene as the only spectroscopically observable product (Figure 6c). Reduction of the catalyst loading to 0.0002 mol% gave 11% conversion to azoxybenzene as the sole product after 1.5 h at 25 °C; this corresponds to a TON of 55,000 and a

TOF of 37,000 h^{-1} which is probably more representative of the potential intrinsic turnover rate of the catalyst. The composition/selectivity-time profile for the $NaBH_4$-mediated selective partial reduction of nitrobenzene to azoxybenzene in ethanol catalyzed by 0.005 mol% **3a-PEG** in Figure 7 shows that azoxybenzene is the only observable product and that 100% selectivity is retained even at complete conversion (150 min); however, longer reaction times resulted in a slight drop in selectivity due to the formation of aniline. While we are not sure whether this aniline forms via hydrolysis of the azoxybenzene and reduction of the resulting *N*-phenylhydroxylamine (i.e. the direct pathway) or via azobenzene and 1,2-diphenylhydrazine (condensation pathway), we tentatively suggest that the direct pathway operates under these conditions as we have not observed any other intermediates from the condensation pathway. To this end, a recent experimental and computational investigation on the ruthenium nanoparticle catalyzed reduction of nitrobenzene has succinctly demonstrated that even when azoxybenzene forms aniline is still likely to be generated via the direct pathway as formation of Ph-NH-N-OH-Ph and Ph-NH-NH-Ph are both thermodynamically difficult uphill processes.[13] In comparison to **3a.PEG**, **3a** also catalyzed the reduction of nitroarenes in ethanol with high selectivity for azoxybenzene, but only reached 29% conversion in the same time; this again may well reflect the accessibility of the active site arising from the disparate hydrophilicity and dispersibility of these catalysts The influence of the phosphorus heteroatom donor on catalyst selectivity was also examined by comparing the performance of AuNP@PEG-PIILP and AuNP@PIILP under the same conditions. Selective removal of the PPh_2 resulted in a marked drop in activity as well as a reduction in selectivity with AuNP@PEG-PIILP giving 26% conversion and 88% selectivity while AuNP@PIILP reached 23% conversion and 65% selectivity for azoxybenzene. Finally, the efficacy of **3a.PEG** was further compared against AuNP@citrate which catalyzed the reduction under the same conditions but only reached 13% conversion after 3 days albeit with 100% selectivity for azoxybenzene.

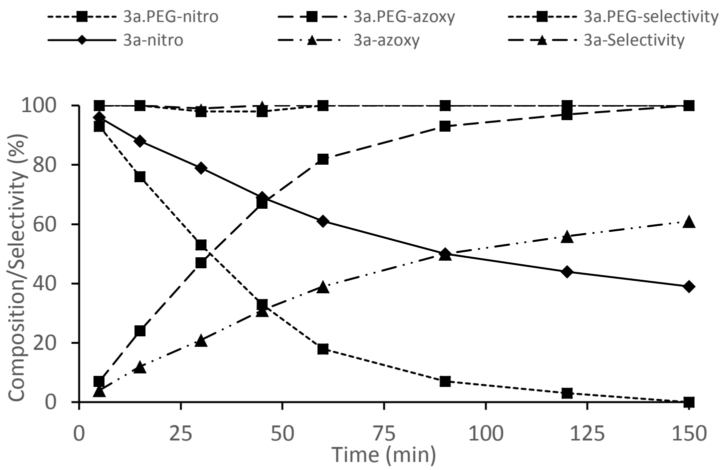


Figure 7 Reaction profile and azoxybenzene selectivity as a function of time for the partial reduction of nitrobenzene to azoxybenzene in ethanol at 25 °C using 2.5 equivalents of $NaBH_4$ and catalyzed by 0.005 mol% **3a** and **3a**.**PEG**.

As the reductions in water and ethanol were conducted under otherwise identical conditions, we tentatively suggest that the switch in selectivity may be associated with the markedly higher solubility of nitrobenzene in ethanol compared with water as this would result in a higher concentration of reactant on the surface of the nanoparticle which would favor condensation of two reactive species.

Complete selectivity for azoxybenzene with such a TOF under mild conditions is quite remarkable and unprecedented for a gold nanoparticle catalyst. Indeed, a survey of the literature revealed that there are a limited number of catalysts capable of reducing nitrobenzene to azoxybenzene and in each case both **3a** and **3a-PEG** outperformed these by quite some margin. For example, gold nanoparticles supported on mesostructured ceria (Au/*meso*-CeO_2) is a selectivity switchable catalyst that reduces nitroarenes with 2-propanol to the azoxyarene, azoarene and the corresponding aniline depending on the reaction conditions.[36b] However, a much higher catalyst loading (1 mol%) and longer reaction times were required and the TOF of 20 h^{-1} was significantly lower than that of 37,000 h^{-1} reported above for **3a.PEG**. Most interestingly, the high selectivity for azoxyarene was obtained in 2-propanol and addition of water resulted in a switch in selectivity to afford azoxyarene; this is in stark contrast to **3a** and **3a.PEG** which generated N-phenylhydroxylamine as the sole product in a 1:1 mixture of 2-propanol and water. Other systems that catalyze the selective reduction of nitrobenzene include urchin-like Ni/graphene nanocomposites that reached 100% selectivity but with a TOF of only 16.8 h^{-1},[36c] Ag-Cu alloy nanoparticles that catalyze selective reduction of nitroarenes to azoxy compounds through visible light irradiation with good selectivity (76-86%) but low TOFs (1-2 h^{-1})[36d] and iridium/rhodium-based hierarchically-coiled ultrathin nanosheets that gave azoxybenzene up to 89% selectivity and a TOF of 400 h^{-1}.[36e]

As the majority of AuNP-based systems catalyze the reduction of nitroarenes to afford the corresponding aniline, studies were undertaken with catalyst **3a** and **3a.PEG** to establish the conditions necessary to achieve complete reduction to aniline with the aim of comparing and evaluating their efficacy against existing systems. Using the studies described above as a lead, the reduction of nitrobenzene was monitored as a function of time at 60 °C in water using 0.005 mol% **3a.PEG** and the composition quantified by ^{1}H NMR spectroscopy and GC. The resulting composition-time profile shown in Figure 8a shows rapid consumption of nitrobenzene with concomitant formation of *N*-phenylhydroxylamine, which is the major species after 10 min (82%), together with a minor amount of aniline (14%). Longer reaction times resulted in consumption of *N*-phenylhydroxylamine to afford aniline which was ultimately obtained in quantitative yield after 180 min. Not surprisingly, the corresponding composition-time profile obtained with catalyst **3a** is qualitatively similar (Figure 8b) although complete conversion to aniline required significantly longer. Both composition-time profiles are indicative of reaction via the direct pathway as there is no evidence for the formation of azoxy intermediates. In stark contrast, azoxybenzene, diphenylhydrazine and *N*-phenylhydroxylamine have all been identified during the reduction of nitrobenzene with gold nanoparticles supported on imidazolium-based porous organic polymers; however, these studies appear to have been conducted in air which may be the origin of the vastly disparate composition profiles.[26r] Finally, when the catalyst loading was reduced to 0.0002 mol% complete reduction to aniline could be obtained after only 8 h at 50 °C, this corresponds to a TON of 500,000 and a TOF of 62,500 h^{-1} (based on total gold content). Although the poor solubility of the substrate undoubtedly limits this TOF, comparison with related NP-based systems that also operate under mass transfer control reveals it to be among the most active gold nanoparticle-based systems to be reported for the aqueous phase transfer hydrogenation of nitroarenes. The efficacy of **3a.PEG** may well be associated with the electrostatic potential around the AuNPs as favorable electrostatic interactions between positively charged ([+])-AuNPs and negatively charged substrates has been demonstrated to be responsible for enhancing the rate of reduction of nitroarenes by channeling the substrate to the NP surface.[47a] In this system, AuNPs modified with positively charged thiolates, ([+])-AuNP, gave complete reduction of 4-nitrophenolate and 4-nitroaniline at room temperature in only 10 min with a catalyst loading of 0.1 mol% whereas its negatively charged counterpart ([-]) AuNPs failed to catalyze the same reductions even after 2 days. In a related concept, the approach of charged substrates such as nitroarenes to the surface of a nanoparticle catalyst has recently been reported to be controlled by the size of the counterions surrounding charged on-particle ligands.[47b]

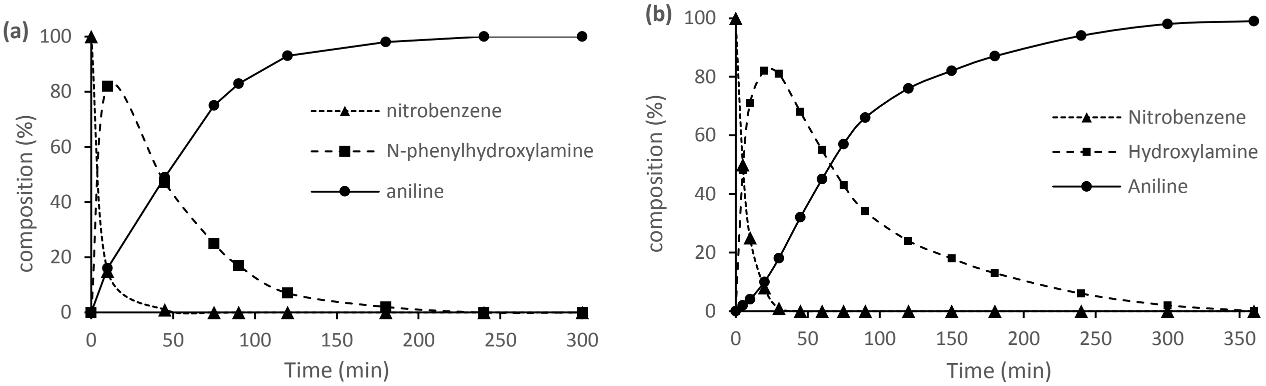
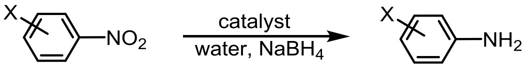
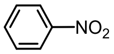
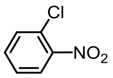
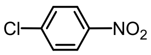
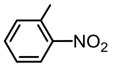
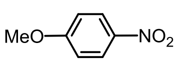
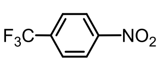
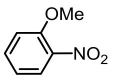
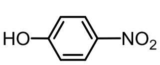
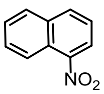


Figure 8 Reaction profiles as a function of time for the reduction of nitrobenzene in water under nitrogen at 60 °C using 5.0 mole equivalents of $NaBH_4$ showing direct reduction to aniline via *N*-phenylhydroxylamine to be the major pathway (a) 0.005 mol% **3a.PEG** and (b) 0.005 mol% **3a**.

The protocol developed above for reduction of nitrobenzene to aniline has also been extended to a selection of electron rich and electron poor substrates which all gave high conversion to afford the corresponding aniline as the sole product after relatively short reaction times (4-6 h) (Table 3). Gratifyingly, reduction of 1-chloro-4-nitrobenzene and 1-chloro-2-nitrobenzene occurred with high selectivity to afford 4-chloro and 2-chloroaniline, respectively, with no evidence for hydrodechlorination to afford aniline. Nitroarenes substituted at the 2-position were also converted to the corresponding aniline in high yield and 100% selectivity, albeit after slightly longer reaction times due to steric hindrance inhibiting access of the substrate to the catalyst surface. Similarly, while reduction of 1-nitronaphthalene was sluggish under the same conditions, complete conversion to 1-aminonaphthalene could be obtained after only 6 h when the reaction temperature was raised to 70 °C.

Table 3 Sodium borohydride mediated reduction of nitroarenes to the corresponding aniline catalyzed by AuNP@PPh2-PEGPIILP (**3a.PEG**).[a]



substrate	Time	Conv. (%)/Select. (%)[b]
	2h	99/100
	5h	100/100
	5h	100/100
	5h	99/100
	4h	98/100
	5h	98/100
	6h	97/99
	4h	100/100
	6h	>99/100

[a] Reaction conditions: 1 mmol substrate, 0.005 mol% **3a.PEG**, 2.0 mL water, 5.0 mmol $NaBH_4$, 50 °C, reaction time given in parentheses after conversions (h). [b] Yields determined by ^{1}H NMR spectroscopy using dioxane as internal standard. Average of three runs.

CONCLUSIONS

Gold nanoparticle catalysts stabilized by phosphine-decorated polymer immobilized ionic liquids are exceptionally efficient catalysts for the partial and complete reduction of nitrobenzene and give unprecedentedly high activities and selectivities for *N*-phenylhydroxylamine, azoxybenzene and aniline. Reductions conducted in water under mild conditions at low catalyst loadings afford *N*-phenylhydroxylamine in quantitative yields and >99% selectivity while the use of ethanol as solvent, under otherwise identical conditions, results in a dramatic switch in selectivity to afford azoxybenzene as the sole product. The composition-selectivity profiles for the partial reduction of nitrobenzene raises a number of searching and pertinent questions about the origin of the selectivity and the mechanism of reduction and further *in situ* surface spectroscopic investigations as well as kinetic and computational studies will be required to develop a full understanding of this system. As both the phosphine and ionic liquid components are required for optimum efficacy future studies on modified catalyst systems will be undertaken to explore whether the electronic structure of the gold nanoparticles and/or the electrostatic potential around the AuNPs are selectivity and activity determining. The modular construction of the PIIL supports will lend itself to modifying properties such as ionic microenvironment and surface potential, the density of heteroatom donors, hydrophilicity, porosity and mechanical integrity and thereby substrate accessibility, catalyst surface interactions and ultimately catalyst efficacy. In particular, PIILP-based systems are ideally suited to explore the role of electrostatic interactions in the reduction of charged substrates with the aim of developing smart catalysts with enzymatic activity and selectivity. We are currently using our optimum catalyst to develop a continuous flow process for the scale-up synthesis of *N*-phenylhydroxylamine and azoxybenzene as both intermediates to industrially important value-added products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.XXXXXXXX

Synthesis and characterization of $AuCl_4$-loaded co-polymers **2a**, **2a.PEG**, **3b** and **2b.PEG**, TGA and DSC curves for **1a**, **1a.PEG**, **1b** and **1b.PEG** (PDF), SEM images for **2a, 2a.PEG, 2b and 2b.PEG** (PDF), TEM images of **3a**, **3a.PEG**, **3b** and **3b.PEG** (PDF), FTIR traces (PDF) and X-ray photoelectron spectra for **2a**, **2a.PEG**, **2b**, **2b.PEG**, **3a**, **3a.PEG**, **3b** and **3b.PEG** (PDF).

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Notes

The authors declare no competing financial interest.

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