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# Improved Stability and Catalytic Activity of Palladium Nanoparticle Catalysts using Phosphine-Functionalized Imidazolium Ionic Liquids

Kylie L. Luska[a] and Audrey Moores[a,*]

[a] Department of Chemistry, McGill University, Otto Maass Chemistry Building, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6
Fax. (+1)-514-398-3797; phone: (+1)-514-398-4654
E-mail: audrey.moores@mcgill.ca

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**Abstract:** Palladium nanoparticles (Pd NPs) stabilized by 6 different phosphine-functionalized ionic liquids (PFILs) were synthesized in imidazolium-based ionic liquids (ILs) using $H_{2(g)}$ (4 bar) as a reductant. Characterization showed well-dispersed particles of ~3 nm (TEM) and confirmed the PFIL stabilization of the NPs (XPS). The PFILs were composed of an imidazolium functionality separated from the phosphine group by a propyl or undecyl chain. The counter anions for both FILs and IL solvents were chosen from *N*-bis(trifluoromethanesulfonyl)imide ($Tf_2N^-$), trifluoromethanesulfonate ($TfO^-$) or hexafluorophosphate ($PF_6^-$). Colloidal suspensions of the Pd NPs were employed as biphasic hydrogenation catalysts for the reduction of the olefinic bond in styrene under mild conditions (50 °C, 4 bar $H_{2(g)}$, 1.5 h). The PFIL-stabilized Pd NPs were effective hydrogenation catalysts and showed superior activity and recyclability over NPs synthesized in the absence of PFILs. Poisoning tests of the Pd NP catalysts and characterization of the electronic properties of the phosphine were also performed.

**Keywords:** biphasic catalysis; functionalized ionic liquids; hydrogenation; ionic liquids; nanoparticles; palladium

## Introduction

Ionic liquids (ILs) have been employed as useful media for the generation of transition metal nanostructures of various sizes and shapes as a result of their ability to act as both a solvent and stabilizing ligand.[1] 1,3-Dialkylimidazolium ILs have been of particular interest since their pre-organized structures provide both a hydrophilic and hydrophobic domain to control the growth of nanoparticles (NPs).[2] The resulting NPs can be isolated from the IL or employed as colloidal suspensions since electrostatic stabilization of the NPs is provided by the IL through the formation of supramolecular species of the form $[(DAI)_x(X)_{x-n}]^{n+}$ and $[(DAI)_{x-n}(X)_x]^{n-}$ (where DAI = 1,3-dialkylimidazolium cation and $X^-$ = counter anion).[2] Imidazolium ILs are interesting species for the synthesis of NPs since changing the nature of the IL (i.e., N-alkyl chain length,[3] counter anion volume)[1c,4] can influence the properties of the resulting NPs.

The most common use of metal NPs embedded in ILs has been in the field of catalysis as the IL allows for a facile separation of the product, through decantation or extraction, and reuse of the IL phase containing the NP catalyst. These NPs possess high catalytic activities and have been used most effectively in the hydrogenation of alkenes[5] and arenes.[4c] The catalytic activity of these NPs is attributed to the ability of the loosely bound IL species to be displaced, which allows the substrate access to catalytically active sites.[2] Although the ILs provide short-term stabilization, their displacement can also lead to aggregation of the metal NPs under catalytic conditions.[5b,6] Further stabilization of metal NPs can be provided by classic transition metal ligands (i.e., bipyridine,[1e,7] phenanthroline),[8] polymers (i.e., poly-vinylpyrrolidone,[9] IL co-polymers)[10] or various supports ($SiO_2$,[11] carbon nanotubes)[12] and provide systems possessing increased stabilities, while maintaining high catalytic activities.

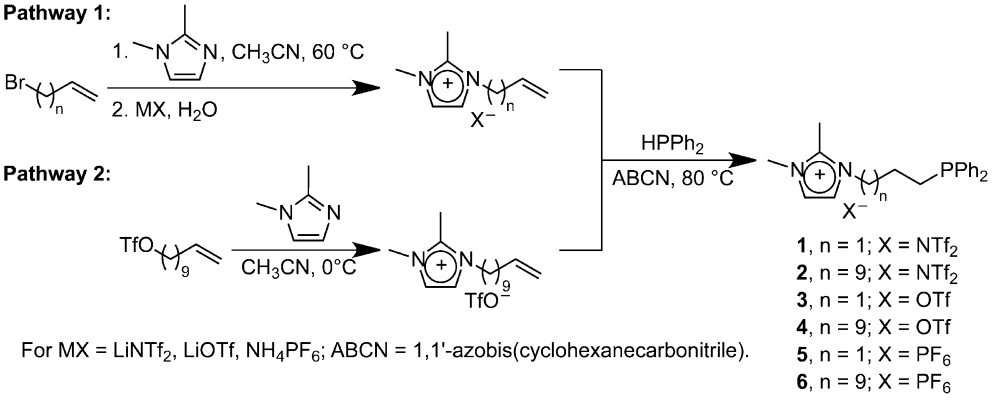
Functionalized ILs (FILs) containing such metal-binding moieties as amines,[12b,13] bipyridine,[6,7c,d,14] carboxylates,[12b] nitriles[15] or thiolates[16] have been previously employed in the synthesis of transition metal NPs. FILs are effective stabilizing ligands since they provide both a covalent and an electrostatic stabilization, while non-functionalized ILs can only provide an electrostatic stabilization to the NPs. Covalent binding of FILs to the NP surface would also influence the electronic properties of the metal as a result of the interaction with the binding moiety and the presence of the highly polar IL layer surrounding the NP. In the context of catalysis, this effect could lead to a change of the electron density at the surface metal atoms and/or control of the solubility of substrates at the metal surface, providing both highly active and selective catalytic systems.[7c] In addition to improving NP stability, FIL-stabilized NPs can provide highly recyclable biphasic catalytic systems alleviating difficulties with aggregation of NPs and leaching of metal or organic species into the organic phase.[7c] Several strategies have employed FILs in the synthesis of NPs including: the use of FILs as both a reaction solvent and NP stabilizer,[15] the incorporation of FIL-stabilized NPs onto carbon nanotubes or fibers[12b,c,14,16a] and the use of FILs as an IL-soluble ligand.[6,7c,d] Recently, several groups have employed bipyridine FILs in the synthesis of efficient biphasic hydrogenation NP catalysts.[6,7c,d]

Herein, we report the employment of phosphine-functionalized ionic liquids (PFILs) **1–6** (Scheme 1) as stabilizing ligands in the generation of colloidal suspensions of Pd NPs in imidazolium ILs and their subsequent use as efficient and recyclable biphasic hydrogenation catalysts. Halide-free NPs were synthesized from $Pd(acac)_2$ in [BDMI]X under an atmosphere of $H_{2(g)}$ in the presence of PFILs (Scheme 2). Well-dispersed NPs were characterized by transmission electron microscopic (TEM) and X-ray photoelectron spectroscopic (XPS) analysis, which provided evidence for the PFIL stabilization of the NPs. Pd NPs were employed as olefin hydrogenation catalysts for the conversion of styrene to ethylbenzene. Comparisons between PFIL-stabilized NPs and those obtained without PFIL stabilization demonstrate the superior activity and stability of these systems. Furthermore, the nature of the FIL employed, in terms of the N-alkyl chain length (n) and the anionic species ($X^-$), was shown to influence the catalytic activity of the NPs.

## Results and Discussion

### Synthesis of Phosphine-Functionalized Ionic Liquids

The synthesis of PFILs **1–6** followed a similar procedure to that reported by Dupont and co-workers in which a radical chain addition of diphenylphosphine to alkene FILs was catalyzed by 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) to provide the desired phosphines in almost quantitative yields (Scheme 1).[17] Two pathways were employed to provide a series of alkene FILs in which the length of the N-alkyl chain ($n$), for $n=1$, 9, and the counter anion ($X^-$), for $X^-$ = bis(trifluoromethanesulfonyl)imide ($Tf_2N^-$), trifluoro-




**Scheme 1.** Synthesis of phosphine-functionalized ionic liquids (PFILs) **1–6**.


**Scheme 2.** Formation of PFIL-stabilized palladium nanoparticles in [BDMI]X.

methanesulfonate ($TfO^-$), hexafluorophosphate ($PF_6^-$), were varied. In pathway 1, alkenylimidazolium salts were synthesized through the quaternization of 1,2-dimethylimidazole with alkenyl bromides and a salt exchange with either $LiNTf_2$, LiOTf or $NH_4PF_6$.[17] Pathway 2 was employed to synthesize the undecenylimidazolium $TfO^-$ salt *via* a halide-free methodology involving the quarternization of 1,2-dimethylimidazole with undec-10-enyl trifluoromethanesulfonate.

## Synthesis and Characterization of Palladium Nanoparticles

The synthesis of Pd NPs was achieved through the reduction of $Pd(acac)_2$ (acac = acetylacetonate) in [BDMI]X under an atmosphere of $H_{2(g)}$ (4 bar) in the presence of 1.0 equivalent of PFILs **1–6** (Scheme 2). After reaction for 4 h at 80 °C, the IL transforms from a bright yellow solution to a brown suspension and TEM analysis of the IL phase shows the presence of small, well-dispersed NPs having diameters of ~3 nm (Table 1). A correlation between the size of the Pd NPs and the parameters of the phosphine ligand, in terms of n and $X^-$, was not observed. The NP:IL colloidal suspension was used directly for catalytic studies or the NPs were isolated from the IL by repeated washing using an acetone:pentane (2:1) solution and centrifugation. The [PFIL]/[Pd] molar ratio of 1.0 was selected as a good compromise between stability and activity, whereas a ratio $<1.0$ provided Pd aggregates (Figure 1) and a ratio of 2.0 provided mono-dispersed NPs with dramatically reduced activity. It should be noted that the 1-alkyl-2,3-dimethylimidazolium salts of PFILs **1–6** and [BDMI]X ILs were chosen to prevent the formation of carbene species during NP synthesis and allow for the synthesis of well-defined NPs free of carbene contamination. The formation of 1,3-dialkylimidazolium carbenes has been proposed to serve as stabilizing ligands and/or NP catalyst poisons.[18]

An X-ray photoelectron spectroscopic (XPS) analysis of the Pd NPs was employed to elucidate the nature of the stabilizing layer of the particles. XPS analysis of Pd NPs stabilized by PFIL **3** showed the presence of palladium, phosphorus, fluorine, nitrogen, sulfur, oxygen and carbon, which signified the presence of the PFIL in the ligand sphere of the NPs. The P $2p_{(3/2)}$ binding energy (BE) for PFIL **3**-stabilized NPs (130.9 eV) was comparable to that of PFIL **3** (130.7 eV) (see Supporting Information, Figure S6 and Figure S7). A shift in the XPS spectrum for the Pd–P signal was not expected since the electronegativities of Pd and P are similar. The BEs for Pd, $3d_{(5/2)} = 335.7$ eV and $3d_{(3/2)} = 341.0$ eV, indicated the NPs were composed of Pd(0) (see Supporting Information, Figure S5) and were in agreement with other phosphine-stabilized Pd NPs.[19] The Pd 3*d* spectrum also indicated the presence of Pd–O bonds, which could result from either the oxidation of Pd due to air exposure or due to the interaction of the $TfO^-$ counter anion with the Pd surface (see Supporting Information, Figure S8 and Figure S9).[20] The XPS data suggest that the primary stabilization of the Pd NPs was provided by the phosphine moiety of the PFIL; although, the possible stabilization by the IL anion and/or a metal oxide layer cannot be excluded. To this end, the $TfO^-$ anion could have been provided by either PFIL **3** or the IL solvent and as such the presence of [BDMI]OTf in the ligand layer of the NPs could not be ruled out as contributing to the stabilization of the NPs. XPS analysis of [BDMI]OTf-stabilized Pd NPs was not undertaken since only Pd aggregates were produced and did not provide a comparable sample to our mono-dispersed PFIL-stabilized NPs. However, Dupont and co-workers have reported XPS evidence for IL anion stabilization of NPs synthesized in IL solvents.[5b,20] Small NPs stabilized by

**Table 1.** Particle size and distribution of Pd NPs stabilized by PFILs **1–6** determined by TEM before and after catalysis.[a]

| Solvent | Stabilizing Ligands | | | Particle Size [nm] (standard deviation σ) | |
|---|---|---|---|---|---|
| | PFIL | *n* | X | Before catalysis | After three cycles |
| $[BDMI]NTf_2$ | none[b] | | | aggregates | aggregates |
| | **1** | 1 | $Tf_2N$ | 3.0 (±0.6) | 3.1 (±0.7) |
| | **2** | 9 | $Tf_2N$ | 3.2 (±0.8) | 3.5 (±0.7) |
| [BDMI]OTf | none[b] | | | aggregates | aggregates |
| | **3** | 1 | TfO | 3.5 (±1.0) | 3.7 (±0.8) |
| | **4** | 9 | TfO | 3.0 (±0.6) | 2.8 (±0.7) |
| $[BDMI]PF_6$ | none[b] | | | aggregates | aggregates |
| | **5** | 1 | $PF_6$ | 2.8 (±0.7) | 2.7 (±0.5) |
| | **6** | 9 | $PF_6$ | 2.7 (±0.5) | 2.5 (±0.6) |

[a] *Reaction conditions:* $Pd(acac)_2$ (0.1 mmol), PFIL **1–6** (0.1 mmol), [BDMI]X (2.0 mL), $H_{2(g)}$ (4 bar), 80 °C, 4 h, stirred at 1000 rpm.
[b] Identical reaction conditions without the addition a PFIL stabilizer.

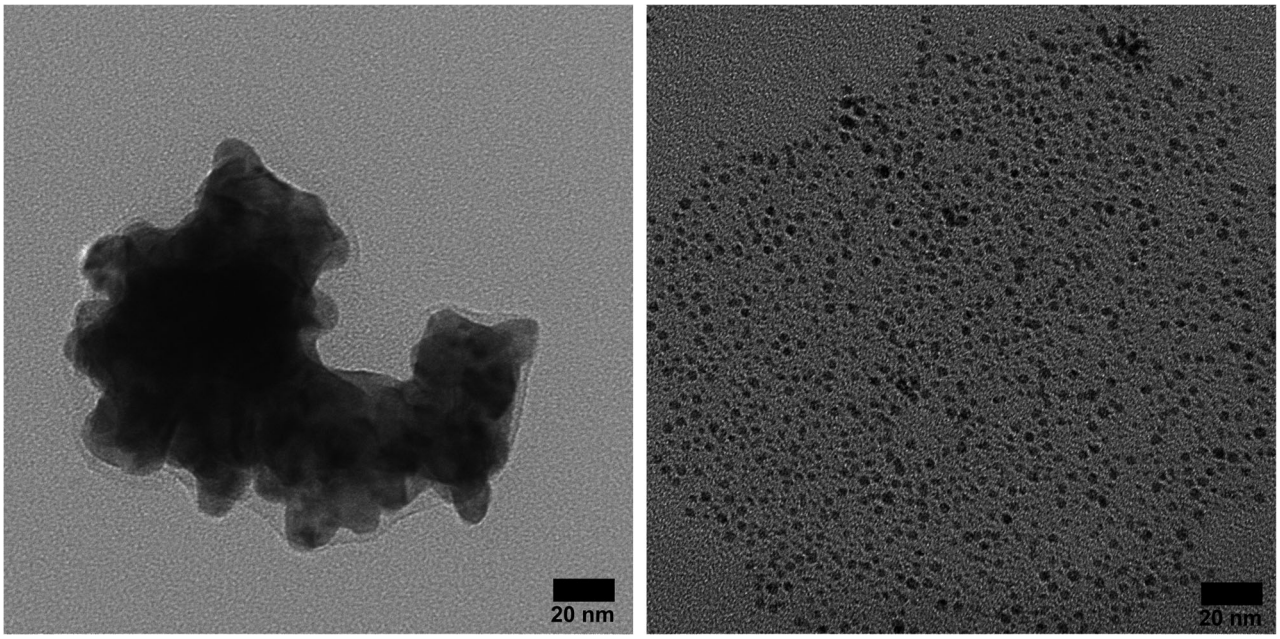



**Figure 1.** TEM micrographs of Pd NPs synthesized in [BDMI]$NTf_2$ employing 0.0 equiv. of PFIL (*left*) and 1.0 equiv. of PFIL **1** (*right*).

IL solvents containing either $BF_4^-$ or $PF_6^-$ anions have shown a metal-fluorine interaction in XPS.

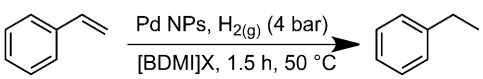
$^{31}P$ NMR studies of PFIL **1** stabilized Pd NPs in [BDMI]$NTf_2$ were conducted. The NPs were synthesized as outlined above employing 1.0 equivalent of PFIL **1** and care was taken to keep the sample under an inert atmosphere. Analysis of the NPs showed only a weak signal at 29.5 ppm (see Supporting Information, Figure S10), which does not correspond to PFIL **1** (−17.6 ppm) (see Supporting Information, Figure S11a) or the PFIL **1** oxide (31.8 ppm) (see Supporting Information, Figure S11b). This signal is consistent with a Pd(II) complex of a diphenyl-(alkyl)phosphine.[21] A $^{31}P$ NMR spectrum of the NPs was taken after the first cycle of styrene hydrogenation (see Supporting Information, Figure S12) and no signal was detected. The disappearance of the species observed at 29.5 ppm correlates well with the reduction of the intermediate Pd complex with PFIL **1** into Pd NPs during the first hydrogenation cycle. In liquid NMR, probed nuclei attached to a surface do not exhibit any signal. All these observations thus indicate that the majority of the phosphine was attached to the NPs surface.

Lastly, the dynamics of the PFIL **1**-stabilized NPs were investigated using $^{31}P$ NMR. Heating a sample of PFIL **1**-stabilized NPs to either 50 or 75 °C (see Supporting Information, Figure S13 and Figure S14) did not change the spectrum (i.e., liberate free PFIL **1** from the NPs). Addition of greater equivalents of PFIL **1**, 1.0, 2.0 or 4.0 equivalents with respect to Pd (see Supporting Information, Figure S15 to Figure S23), caused the formation of a broad signal at −17.8 ppm corresponding to free phosphine. Heating these samples to 50 or 75 °C caused the broadening or complete disappearance of the free phosphine signal. These two points indicate that an exchange process between free PFIL and the PFIL-stabilized NPs is occurring and demonstrates the lability of the ligand. In the context of catalysis, this lability would allow the Pd NPs to be stable against aggregation while creating active sites during catalysis to provide effective catalyst systems.

## Styrene Hydrogenation Employing Palladium Nanoparticles

The catalytic properties of Pd NPs stabilized by PFILs **1–6** were tested by use in the biphasic olefin hydrogenation of styrene (Scheme 3). The PFIL-stabilized Pd NPs embedded in [BDMI]X were efficient catalysts for the reduction of styrene to ethylbenzene under mild conditions (50 °C, 4 bar $H_{2(g)}$, 1.5 h). Aromatic hydrogenation of styrene to ethylcyclohexane was not observed under these reaction conditions.

The NP:IL mixtures were reused for consecutive hydrogenation cycles after pentane extraction and




**Scheme 3.** Reaction conditions for the hydrogenation of styrene employing Pd NPs stabilized by PFILs **1–6**.

**Table 2.** Catalytic activity of palladium nanoparticles stabilized by PFILs **1–6** for the hydrogenation of styrene.[a]

| Solvent | Stabilizing Ligands | | | Styrene Conversion [%][b] | | |
|---|---|---|---|---|---|---|
| | PFIL | *n* | X | Cycle 1 | Cycle 2 | Cycle 3 |
| $[BDMI]NTf_2$ | blank[c] | | | 23 | 31 | 37 |
| | **1** | 1 | $Tf_2N$ | 85 | 100 | 100 |
| | **2** | 9 | $Tf_2N$ | 73 | 83 | 85 |
| [BDMI]OTf | blank[c] | | | 18 | 21 | 26 |
| | **3** | 1 | TfO | 48 | 79 | 78 |
| | **4** | 9 | TfO | 46 | 61 | 70 |
| $[BDMI]PF_6$ | blank[c] | | | 30 | 31 | 28 |
| | **5** | 1 | $PF_6$ | 28 | 52 | 65 |
| | **6** | 9 | $PF_6$ | 52 | 73 | 70 |

[a] *Reaction conditions:* $Pd(acac)_2$ (0.1 mmol), PFIL **1–6** (0.1 mmol), [BDMI]X (2.0 mL), styrene (25.0 mmol), $H_{2(g)}$ (4 bar), 50 °C, 1.5 h, stirred at 1000 rpm.
[b] Determined by GC analysis employing dodecane as internal standard.
[c] Identical reaction conditions without the addition a PFIL stabilizer.

drying under vacuum for at least 1 h. As outlined in Table 2, each NP catalyst was employed for three consecutive hydrogenation cycles of styrene; the catalytic activity of the Pd NPs was observed to increase upon recycling for both PFIL and [BDMI]X-stabilized catalysts. This induction period could result from: (i) an incomplete reduction of the Pd(II) precursor, which allowed the continued formation of Pd NPs during the initial hydrogenation cycles; or (ii) a restructuring of the NPs under catalytic conditions to provide more active catalytic sites. The latter phenomenon has been reported by Janiak and co-workers for [1-butyl-3-methylimidazolium]X-stabilized NPs, which exhibited an increase in the initial rate of cyclohexene hydrogenation with recycling.[5a,22] The increased activity was attributed to the restructuring of the metal surface and/or the formation of N-heterocyclic carbene (NHC) surface species.[5a,22] In regard to our Pd NPs, the formation of Pd-NHC species is less likely to occur since the 1-alkyl-2,3-dimethylimidazolium salts of PFILs and [BDMI]X were employed. Furthermore, TEM analyses of the NP:IL phase before catalysis and after the third hydrogenation cycle were performed for each catalyst (Table 1) and showed consistent NP sizes before and after three cycles of catalysis. Therefore, the induction period most likely results from the incomplete decomposition of the Pd(II) precursor under the reaction conditions employed for NP synthesis.

Hydrogenation of styrene employing Pd NPs stabilized by PFILs **1–6** were compared against Pd NPs synthesized in [BDMI]X in the absence of a phosphine stabilizer to investigate the influence of the PFIL on catalytic activity. NP:IL mixtures synthesized solely in [BDMI]X were shown to have some catalytic activity (Table 2; entries 1, 3, 5); however, PFIL-stabilized Pd NPs showed a significant increase in catalytic activity (Table 2; entries 2–4, 6/7, 8/9). As mentioned above, NP synthesis in the presence of PFILs **1–6** provided well-dispersed NPs, while the synthesis without PFIL yielded a mixture of small NPs and large aggregates. The increased activities for PFIL-stabilized NPs were attributed to an increase in the number of catalytically active sites for PFIL-stabilized NPs resulting from a larger surface-to-volume ratio of the smaller Pd NPs.

Both the N-alkyl chain length and the counter anion of the PFIL ligands were shown to influence the catalytic activity of the resulting Pd NPs. The nature of the PFIL counter anion ($X^-$) affected the activity of the NPs greatly as the $Tf_2N^-$ PFILs **1** and **2** possessed a higher catalytic activity then the $TfO^-$ or $PF_6^-$ PFILs **3–6**. The most active catalyst was PFIL **1**-stabilized Pd NPs as complete conversion of styrene was achieved during the second and third hydrogenation cycles (Table 2; entry 2). Increased activity for the $Tf_2N^-$-based catalyst could result from the increased hydrophobicity of PFIL **1** and $[BDMI]NTf_2$, as both $TfO^-$- and $PF_6^-$-based ILs are known to be more hydrophilic.[23] It was also observed that the length of the N-alkyl chain (n) influenced the activity of the NPs; although, to a lesser extent than that of the counter anion. In the case of the $Tf_2N^-$-based PFILs **1** ($n=1$) and **2** ($n=9$), the longer chain PFIL **2** possessed a lower catalytic activity than the shorter chain PFIL **1**. The lower catalytic activity could result from an increase in the hydrophobicity of the ligand sphere, which would increase the solubility of styrene or ethylbenzene at the Pd surface and thus hinder access to catalytically active sites.

The long-term stability of the NP catalysts was also evaluated over ten consecutive hydrogenation cycles for the hydrogenation of styrene employing the most active catalysts based on the short N-alkyl chain phosphines, PFIL **1**, **3** and **5** (see Supporting Information, Figure S1). PFIL **1** stabilized NPs were again the most active catalyst over the series of ten hydrogenation cycles. In comparison, PFIL **3** provided slightly

lower styrene conversions, while the activity of PFIL **5** stabilized NPs was significantly lower. The average styrene conversions over the ten hydrogenation cycles were: 85, 61 and 38% for PFIL **1**, **3**, and **5** respectively. TEM was employed to analyzes the NP:IL phase after ten runs and showed Pd NPs sizes of 3.3(±0.9), 3.8(±0.7) and 2.6(±0.4) nm for PFIL **1**, **3** and **5**, respectively. These diameters were similar to those observed before and after the third cycle of catalysis (Table 1).

In view of the $^{31}$P NMR studies outlined above, a catalyst poison test employing $CS_2$ was performed to determine whether the active catalyst species was heterogeneous. The addition of 0.5 equivalents (w.r.t. Pd) of $CS_2$ to the NP:IL mixture completely deactivated the catalyst such that no ethylbenzene was formed under typical hydrogenation conditions for Pd NPs stabilized by PFIL **1**. Therefore, this indicated that the residual Pd complex that was present after NP synthesis was not the active catalyst species.

## Characterization of the Electronic Properties of Phosphine-Functionalized Ionic Liquids

Functionalization of phosphine ligands with ionic moieties has been a popular strategy in the development of biphasic catalysts since the use of tris(3-sulfophenyl)phosphine trisodium salt (TPPTS) in the Ruhrchemie/Rhône–Poulenc process.[24] Important to this field in the context of catalysis is the influence, both steric and electronic, that the ionic group has on the coordination chemistry of the phosphine moiety. The steric effect of a phosphine is often evaluated by the Tolman cone angle, while the electronic influence can be estimated from the synthesis the phosphine selenides or the metal carbonyl complexes.[24b] To this end, the influence of the PFIL parameters (i.e., N-alkyl chain length and counter anion) on the electronic properties of the phosphine moiety were determined through the synthesis of the corresponding phosphine selenides and rhenium carbonyl complexes.

## Synthesis of Phosphine Selenides

The electronic properties of phosphines can be evaluated from the $^1J_{P,Se}$ coupling constant in the $^{31}$P NMR of the corresponding phosphine selenide. Allen and co-workers have shown that the $^1J_{P,Se}$ coupling constant can be related to the degree of *s*-character in the lone pair of the phosphorus atom and as such stronger σ-donors have smaller $^1J_{P,Se}$ coupling constants.[25] The series of phosphine selenides based on PFILs, **1**, **3**, **5** and **6** was synthesized to determine whether the N-alkyl chain length ($n=1$, 9) or counter anion ($X^- = Tf_2N^-$, $TfO^-$, $PF_6^-$) influenced the electronic parameters of the phosphine. The synthesis involved stirring the PFIL and selenium powder in DMSO-$d_6$ overnight at room temperature. The $^{31}$P NMR of the reaction mixtures showed quantitative conversion of PFILs into the corresponding phosphine selenide (Table 3, see Supporting Information, Figure S24 to Figure S28).

**Table 3.** $^{31}$P NMR data for the phosphine selenides of PFILs.

| Stabilizing Ligands PFIL | *n* | X | δ [ppm] | $^1J_{P,Se}$ [Hz] |
|---|---|---|---|---|
| **1** | 1 | $Tf_2N$ | 36.2 | 726 |
| **3** | 1 | TfO | 36.2 | 726 |
| **5** | 1 | $PF_6$ | 36.2 | 726 |
| **6** | 9 | $PF_6$ | 36.6 | 722 |

According to the data in Table 3, it was determined that the nature of the counter anion does not influence the electronic properties of the PFILs as **1**, **3**, and **5** had identical $^1J_{P,Se}$ values. The length of the N-alkyl chain has a small influence on the electronics of the phopshine moiety as PFIL **6** had a smaller $^1J_{P,Se}$ than PFIL **5** and is thus a slightly better σ-donor. This comparison also shows that a propyl alkyl chain is of sufficient length to isolate the phosphine moiety from the electron-withdrawing ability of the imidazolium group. Furthermore, the selenide of $PPh_3$ was also synthesized in DMSO-$d_6$ ($^1J_{P,Se}=736$ Hz) and as expected our PFILs are stronger σ-donors than $PPh_3$ due the presence of the alkyl substituent.

## Synthesis of Rhenium Carbonyl Complexes

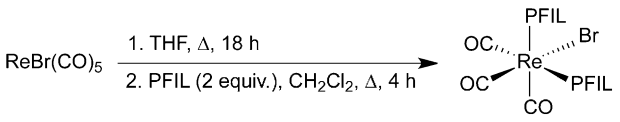
PFILs **1**, **3**, **5** and **6** were also used in the synthesis of Re carbonyl complexes to evaluate the electronic properties of these phosphines through the CO stretching frequencies of these complexes (Table 4). $ReBr(CO)_3(PFIL)_2$ complexes were synthesized in a similar procedure as that reported by Storhoff and Lewis.[26] In short, $ReBr(CO)_5$ was refluxed in THF to produce $[ReBr(CO)_3(THF)]_2$, an intermediate THF complex, which was refluxed in $CH_2Cl_2$ with

**Table 4.** Carbonyl stretching frequencies of $ReBr(CO)_3(PFIL)_2$ complexes.

| Stabilizing Ligands PFIL | *n* | X | CO Stretching Frequency [$cm^{-1}$][a] |
|---|---|---|---|
| **1** | 1 | $Tf_2N$ | 2028, 1946, 1901 |
| **3** | 1 | TfO | 2028, 1944, 1900 |
| **5** | 1 | $PF_6$ | 2022, 1935, 1912 |
| **6** | 9 | $PF_6$ | 2023, 1938, 1897 |

[a] All signals strong and samples recorded as an ATR analysis.




**Scheme 4.** Synthesis of model rhenium complexes.

2.0 equivalents of PFIL to yield the desired *fac*-$ReBr(CO)_3(PFIL)_2$ complex (Scheme 4). $ReBr(CO)_3(PFIL)_2$ complexes of PFIL **1**, **3**, and **5** contain a propyl ($n=1$) chain and allowed for the evaluation of the counter anion. The CO stretching frequencies for the $Tf_2N^-$ (PFIL **1**) and $TfO^-$ complexes (PFIL **3**) were similar, while those of the $PF_6^-$ complex (PFIL **5**) were shifted to lower wavenumbers. This shift indicates that the $PF_6^-$ counter anion interacts with the Re metal center, causing a shift in the CO frequencies. Furthermore, $ReBr(CO)_3(PFIL)_2$ complexes synthesized using PFIL **5** and **6** allowed for the comparison between the short chain ($n=1$) and long chain ($n=9$) PFILs, respectively. CO stretching frequencies for $ReBr(CO)_3$(PFIL **6**)$_2$ were shifted to lower wavenumbers compared to $ReBr(CO)_3$(PFIL **1**)$_2$ or $ReBr(CO)_3$(PFIL **3**)$_2$; however, the shift was not as great as that observed for $ReBr(CO)_3$(PFIL **5**)$_2$. Therefore, the $PF_6^-$ anion interacts with the Re center regardless of the length of the alkyl chain; although, this interaction decreases as the length of the alkyl chain of the PFIL is increased. Taking this finding and that of the phosphine selenides into account, it can be concluded that the electronic properties of the phosphine moiety are not significantly influenced by changes to either $n$ or $X^-$ of the PFILs.

The model Re complexes provide insight into the catalytic activity of the $PF_6^-$ PFILs **5** and **6** (Table 2). These complexes evidenced a possible interaction between the $PF_6^-$ anion and the Re metal center, which can also be envisaged to occur within the ligand sphere of the Pd NPs. As discussed above, Dupont and co-workers have evidenced an interaction between $BF_4^-$ and $PF_6^-$ IL anions with the surface of metal NPs synthesized in IL solvents.[5b,20] This interaction could explain the reduced catalytic activity of NPs stabilized by PFILs **5** and **6** as the $PF_6^-$ anion could occupy catalytically active sites on the Pd surface.

## Conclusions

PFIL-stabilized Pd NP suspensions were used as active and reusable biphasic hydrogenation catalysts for the reduction of olefins. Development of PFILs as effective NP stabilizing ligands has extended the classes of FILs that have been explored and provides an alternative class of ligand that can be used to alleviate particle aggregation issues observed in the synthesis and application of metal NPs in non-functionalized ILs. Furthermore, the N-alkyl chain length and the counter anion of the PFILs have been shown to influence the catalytic activity of the resulting NPs.

## Experimental Section

### General

All syntheses were carried out under an argon atmosphere employing Schlenk techniques. [1-Allyl-2,3-dimethylimidazolium]Br,[17] [1-allyl-2,3-dimethyl-imidazolium]$NTf_2$[17] and PFIL **1**[17] were prepared following known literature procedures. Acetonitrile (dried over 4 Å molecular sieves), allyl bromide (filtration through basic alumina), dichloromethane (distillation over calcium hydride), diethyl ether (distillation over sodium and benzophenone), pyridine (distillation over calcium hydride), and tetrahydrofuran (Grubbs apparatus) were purified prior to use. All other chemicals and solvents were purchased from commercial sources and used without further purification. Melting points (mp) were determined on a Gallenkamp melting point apparatus and are uncorrected. FT-infrared spectra were measured on a Perkin–Elmer Spectrum 400 Spectrometer equipped with a Pike GladiATR. Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Varian Mercury spectrometer. $^1H$ and $^{13}C$ NMR spectra were calibrated to TMS using the residual solvent signal and $^{31}P$ NMR spectra were calibrated using 85% $H_3PO_4$. Mass spectra (MS) were recorded in positive electrospray mode with an IonSpec 7.0 tesla FTMS (Lake Forest, CA). Transmission electron microscopy (TEM) was performed on a Philips CM 200 microscope. X-ray photoelectron spectrometry (XPS) was performed on a VG ESCALAB 3 MKII spectrometer (VG, Thermo Electron Corporation, UK) equipped with an MgKα source. High-pressure experiments were performed employing a Parr Instruments 5000 Series Multiple Reactor System equipped with 100 mL reaction vessels.

### Synthesis of Phosphine Functionalized Ionic Liquids

**1-Allyl-2,3-dimethylimidazolium trifluoromethanesulfonate:** 1-Allyl-2,3-dimethyl-imidazolium bromide (5.78 g, 26.6 mmol) was dissolved in 25 mL $H_2O$ and LiOTf (4.35 g, 27.9 mmol) was added in small portions to the solution. The mixture was stirred at room temperature for 18 h. The aqueous solvent was removed, the crude product was dissolved in MeCN, filtered through celite, dried over $MgSO_4$ and solvent removed to afford a white solid; yield: 4.49 g (59%); mp 44–45 °C. $^1H$ NMR (300 MHz, $CD_3OD$): $\delta=7.50$ (d, $J=2.0$ Hz, 1H), 7.48 (d, $J=2.0$ Hz, 1H), 6.08–5.95 (m, 1H), 5.30 (dd, $J=46.5$, 13.5 Hz, 2H), 4.84–4.78 (m, 2H), 3.83 (s, 3H), 2.60 (s, 3H); $^{13}C$ NMR (75.5 MHz, $CD_3OD$): $\delta=146.3$ (s), 132.0 (s), 123.8 (s), 122.4 (s), 121.9 (q, $J_{C,F}=318.6$ Hz), 120.2 (s), 51.6 (s), 35.6 (s), 9.6 (s); ESI/MS(+): $m/z=$ 137.1073, calcd. for $[C_8H_{13}N_2]^+$: 137.1075.

**1-Allyl-2,3-dimethylimidazolium hexafluorophosphate:** 1-Allyl-2,3-dimethylimidazolium bromide (5.37 g, 24.7 mmol) was dissolved in 25 mL $H_2O$ and $NH_4PF_6$ (4.43 g, 27.9 mmol) was added in small portions to the solution. The mixture was stirred at room temperature for 18 h and ex-

tracted with $CH_2Cl_2$ (50 mL). The organic layer was separated, washed with $H_2O$ (3×50 mL) and dried over $MgSO_4$. Upon solvent removal, the product was dried under vacuum for 18 h at 50 °C to afford an off-white solid; yield: 4.59 g (66%); mp 39–40 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.14 (d, $J$ = 1.0 Hz, 1H), 7.12 (d, $J$ = 2.1 Hz, 1H), 5.95–5.70 (m, 1H), 5.16 (dd, $J$ = 37.0, 13.7 Hz, 2H), 4.57 (d, $J$ = 5.6 Hz, 2H), 3.65 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 144.6 (s), 130.3 (s), 122.5 (s), 121.0 (s), 120.1 (s), 50.4 (s), 34.9 (s), 8.9 (s); ESI/MS(+); $m/z$ = 137.1074, calcd. for $[C_8H_{13}N_2]^+$: 137.1073.

**Undec-10-enyl trifluoromethanesulfonate:** 10-Undecen-1-ol (9.0 mL, 44.9 mmol) and pyridine (4.3 mL, 53.9 mmol) were dissolved in 30 mL of dry $CH_2Cl_2$ and stirred for 15 min. Trifluoromethanesulfonic anhydride (8.3 mL, 49.4 mmol) was dissolved in 40 mL $CH_2Cl_2$ and cooled to 0 °C. The alcohol solution was added dropwise to the cooled solution over 30 min. After stirring for 30 min at room temperature, the mixture was washed with 1 M HCl, water and dried over $MgSO_4$. The solvent was removed and the crude product was purified on silica gel (5% EtOAc:hexanes) to afford a pale yellow liquid; yield: 10.5 g (77%). $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ = 5.79 (m, 1H), 4.93 (m, 2H), 4.51 (t, $J$ = 6.5 Hz, 2H), 2.02 (q, $J$ = 7.1 Hz, 2H), 1.81 (quintet, $J$ = 7.0 Hz, 2H), 1.33 (m, 12H); $^{13}$C NMR (75.5 MHz, $CD_3OD$): $\delta$ = 139.3 (s), 118.9 (q, $J_{C,F}$ = 319.6 Hz), 114.4 (s), 78.0 (s), 34.0 (s), 29.5 (m, 3C), 29.2 (s), 29.1 (s), 29.0 (s), 25.3 (s).

**1-(Undec-10-enyl)-2,3-dimethylimidazolium trifluoromethanesulfonate:** 1,2-Dimethylimidazole (3.28 g, 34.1 mmol) was dissolved in 30 mL of dry MeCN and cooled to 0 °C. Undec-10-enyl trifluoromethanesulfonate (10.3 g, 34.1 mmol) was dissolved in 20 mL of dry MeCN. This solution was added dropwise to the cooled imidazole solution over 5 min. The mixture was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for 18 h. The solvent was removed and the product was dried under vacuum to afford a pale yellow liquid; yield: 12.9 g (95%). $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ = 7.51 (d, $J$ = 2.1 Hz, 1H), 7.46 (d, $J$ = 2.1 Hz, 1H), 5.80 (m, 1H), 4.96 (m, 2H), 4.14 (t, $J$ = 7.5 Hz, 2H), 3.81 (s, 3H), 2.62 (s, 3H), 2.04 (q, $J$ = 6.6 Hz, 2H), 1.81 (quintet, $J$ = 7.1 Hz, 2H), 1.34 (m, 12H); $^{13}$C NMR (75.5 MHz, $CD_3OD$): $\delta$ = 145.9 (s), 140.2 (s), 123.7 (s), 122.3 (s), 121.9 (q, $J_{C,F}$ = 318.4 Hz), 114.9 (s), 49.6 (s), 35.5 (s), 30.9 (s), 30.6 (m, 2C), 30.3 (m, 2C), 30.2 (s), 27.5 (s), 9.6 (s); ESI/MS(+): $m/z$ = 249.2325, calcd. for $[C_{16}H_{29}N_2]^+$: 249.2324.

**1-(Undec-10-enyl)-2,3-dimethylimidazolium bromide:** 1,2-Dimethylimidazole (1.14 g, 11.9 mmol) was dissolved in degassed $CH_3CN$ (12 mL) and 11-bromo-1-undecene (2.60 mL, 11.9 mmol) was added dropwise. The reaction mixture was stirred at 70 °C for 18 h. The solvent was removed to yield an off-white solid, which was suspended in $Et_2O$ (3×50 mL) to wash the crude product. The product was collected and dried under vacuum; yield: 3.18 g (81%); mp 74–75 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70 (d, $J$ = 2.1 Hz, 1H), 7.41 (d, $J$ = 2.1 Hz, 1H), 5.77 (ddt, $J$ = 16.9, 10.1, 6.7, 1H), 5.00–4.86 (m, 2H), 4.16 (t, $J$ = 7.5 Hz, 2H), 4.01 (s, 3H), 2.79 (s, 3H), 2.00 (q, $J$ = 7.0 Hz, 2H), 1.79 (pentet, $J$ = 7.0 Hz, 2H), 1.38–1.19 (m, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 144.0 (s), 139.3 (s), 123.3 (s), 121.1 (s), 114.4 (s), 49.3 (s), 36.5 (s), 34.0 (s), 30.0 (s), 29.5 (s), 29.5 (s), 29.2 (s), 29.2 (s), 29.0 (s), 26.6 (s), 11.3 (s); ESI/MS(+): $m/z$ = 249.2330, calcd. for $[C_{16}H_{29}N_2]^+$: 249.2325.

**1-(Undec-10-enyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide:** 1-(Undec-10-enyl)-2,3-dimethylimidazolium bromide (4.77 g, 14.5 mmol) was dissolved in $H_2O$ (50 mL). Lithium bistrifluoromethanesulfonimidate (4.37 g, 15.2 mmol) was added in portions and the mixture was stirred vigorously for 18 h. The mixture was extracted with $CH_2Cl_2$ (50 mL), washed with $H_2O$ (3×50 mL) and dried over $MgSO_4$. Upon solvent removal, the product was dried under vacuum to afford a yellow liquid; 6.43 g (84%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.16 (d, $J$ = 2.1 Hz, 1H), 7.12 (d, $J$ = 2.2 Hz, 1H), 5.76 (ddt, $J$ = 17.1, 10.2, 6.8, 1H), 5.01–4.80 (m, 2H), 3.98 (t, $J$ = 7.5 Hz, 2H), 3.74 (s, 3H), 2.54 (s, 3H), 1.99 (q, $J$ = 7.0 Hz, 2H), 1.73 (pentet, $J$ = 7.0 Hz, 2H), 1.48–1.09 (m, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 143.6 (s), 139.1 (s), 122.5 (s), 120.7 (s), 119.7 (q, $J_{C,F}$ = 321.6 Hz), 114.1 (s), 48.8 (s), 35.2 (s), 33.7 (s), 29.5 (s), 29.2 (s), 29.2 (s), 29.0 (s), 28.9 (s), 28.8 (s), 26.2 (s), 9.5 (s); ESI/MS(+): $m/z$ = 249.2329, calcd. for $[C_{16}H_{29}N_2]^+$: 249.2325.

**1-(Undec-10-enyl)-2,3-dimethylimidazolium hexafluorophosphate:** 1-(Undec-10-enyl)-2,3-dimethylimidazolium hexafluorophosphate was prepared as outlined for 1-(undec-10-enyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)-amide employing $NH_4PF_6$ in place of $LiNTF_2$ to afford an off-white solid; yield: 3.22 g (86%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.48 (d, $J$ = 2.1 Hz, 1H), 7.43 (d, $J$ = 2.1 Hz, 1H), 5.80 (ddt, $J$ = 17.0, 10.2, 6.7, 1H), 5.03–4.88 (m, 2H), 4.12 (t, $J$ = 7.5 Hz, 2H), 3.80 (s, 3H), 2.60 (s, 3H), 2.04 (q, $J$ = 6.9 Hz, 2H), 1.81 (pentet, $J$ = 6.0 Hz, 2H), 1.44–1.28 (m, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 145.9 (s), 140.3 (s), 123.7 (s), 122.2 (s), 114.9 (s), 49.6 (s), 35.4 (s), 35.0 (s), 30.9 (s), 30.6 (s), 30.6 (s), 30.3 (s), 30.3 (s), 30.2 (s), 27.4 (s), 9.5 (s); ESI/MS(+): $m/z$ = 249.2324, calcd. for $[C_{16}H_{29}N_2]^+$: 249.2325.

**1-[11-(Diphenylphosphino)undecyl]-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide (PFIL 2):** 1-(Undec-10-enyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide (2.06 g, 3.88 mmol), diphenylphosphine (1.45 g, 7.76 mmol) and 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) (20 mg, 0.08 mmol) were combined in a Schlenk flask. The mixture was stirred at 80 °C for 72 h, during which time ABCN (100 mg, 0.40 mmol) was recharged twice. The volatiles were removed under vacuum and the resulting oil was washed with $Et_2O$ (3×20 mL). The product was dried under vacuum to afford a pale yellow oil; yield: 2.14 g (77%). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ = 7.64 (d, $J$ = 2.1 Hz, 1H), 7.61 (d, $J$ = 2.1 Hz, 1H), 7.44–7.30 (m, 10H), 4.08 (t, $J$ = 7.3 Hz, 2H), 3.74 (s, 3H), 2.57 (s, 3H), 2.12–1.97 (m, 2H), 1.81–1.57 (m, 2H), 1.47–1.09 (m, 16H); $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta$ = 144.2 (s), 138.7 (d, $J_{C,P}$ = 13.9 Hz), 132.3 (d, $J_{C,P}$ = 18.5 Hz), 128.5–128.4 (m, 2C), 122.3 (s), 120.8 (s), 119.5 (q, $J_{C,F}$ = 322.1 Hz), 47.5 (s), 34.6 (s), 30.4 (d, $J_{C,P}$ = 12.7 Hz), 29.2 (s), 28.9 (m, 3C), 28.7 (s), 28.5 (s), 26.7 (d, $J_{C,P}$ = 11.1 Hz), 25.6 (s), 25.5 (d, $J_{C,P}$ = 15.9 Hz), 9.1 (s); $^{31}$P NMR (81 MHz, DMSO-$d_6$): $\delta$ = −16.4 (s); ESI/MS(+): $m/z$ = 435.2930, calcd. for $[C_{28}H_{40}N_2P]^+$: 435.2924.

**1-[3-(Diphenylphosphino)propyl]-2,3-dimethylimidazolium trifluoromethanesulfonate (PFIL 3):** PFIL **3** was synthesized as outline for PFIL **2** to obtain a white powder; yield: 1.92 g (94%); mp 76–78 °C. $^1$H NMR (300 MHz, DMSO-$d_6$):

$\delta = 7.64$ (d, $J = 2.0$ Hz, 1H), 7.60 (d, $J = 2.0$ Hz, 1H), 7.39 (m, 10H), 4.21 (t, $J = 7.0$ Hz, 2H), 3.72 (s, 3H), 2.54 (s, 3H), 2.10 (m, 2H), 1.76 (m, 2H). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.4$ (s, 1C), 137.8 (d, $J_{C,P} = 13.2$ Hz, 1C), 132.4 (d, $J_{C,P} = 19.8$ Hz, 1C), 128.8 (m, 2C), 122.4 (s, 1C), 120.8 (s, 1C), 48.1 (d, $J_{C,P} = 15.5$ Hz, 1C), 34.7 (s, 1C), 26.1 (d, $J_{C,P} = 18.3$ Hz, 1C), 22.9 (d, $J_{C,P} = 12.4$ Hz, 1C), 9.2 (s, 1C); $^{31}$P NMR (81 MHz, DMSO-$d_6$): $\delta = -16.4$ (s); ESI/MS(+): $m/z = 323.1672$, calcd. for $[C_{20}H_{24}N_2P]^+$: 323.1666.

**1-[11-(Diphenylphosphino)undecyl]-2,3-dimethylimidazolium trifluoromethanesulfonate (PFIL 4):** PFIL **4** was synthesized as outlined for PFIL **2** to obtain a colourless oil; yield: 92%. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 7.63$ (d, $J = 2.1$ Hz, 2H), 7.60 (d, $J = 2.1$ Hz, 2H), 7.37 (m, 10H), 4.08 (t, $J = 7.3$ Hz, 2H), 3.73 (s, 3H), 2.56 (s, 3H), 2.04 (t, $J = 6.6$ Hz, 2H), 1.69 (quintet, $J = 6.6$ Hz, 2H), 1.47–1.03 (m, 16H); $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.9$ (s, 1C), 139.3 (d, $J_{C,P} = 14.6$ Hz, 1C), 133.0 (d, $J_{C,P} = 18.6$ Hz, 1C), 129.2 (m, 2C), 123.0 (s, 1C), 121.5 (s, 1C), 121.4 (q, $J_{C,F} = 321.9$ Hz, 1C), 48.2 (s, 1C), 35.3 (s, 1C), 31.1 (d, $J_{C,P} = 12.5$ Hz, 1C), 29.9 (s, 1C), 29.8–29.4 (m, 3C), 29.3 (s, 1C), 29.2 (s, 1C), 27.5 (d, $J_{C,P} = 11.4$ Hz, 1C), 26.5–26.0 (m, 2C), 9.8 (s, 1C); $^{31}$P NMR (81 MHz, DMSO-$d_6$): $\delta = -16.4$ (s); ESI/MS(+): $m/z = 435.2924$, calcd. for $[C_{28}H_{40}N_2P]^+$: 435.2917.

**1-[3-(Diphenylphosphino)propyl]-2,3-dimethylimidazolium hexafluorophosphate (PFIL 5):** PFIL **5** was synthesized as outlined for PFIL **2** to obtain a white solid; yield: 100%; mp 112–113 °C. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 7.61$ (d, $J = 2.0$ Hz, 1H), 7.56 (d, $J = 2.0$ Hz, 1H), 7.43–7.31 (m, 10H), 4.18 (t, $J = 7.0$ Hz, 2H), 3.70 (s, 3H), 2.50 (s, 3H), 2.14–2.04 (m, 2H), 1.84–1.66 (m, 2H); $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.4$ (s, 1C), 137.8 (d, $J_{C,P} = 13.3$ Hz, 1C), 132.4 (d, $J_{C,P} = 18.7$ Hz, 1C), 129.1–128.5 (m, 2C), 122.4 (s, 1C), 120.8 (s, 1C), 48.2 (d, $J_{C,P} = 15.0$ Hz, 1C), 34.6 (s, 1C), 26.1 (d, $J_{C,P} = 18.2$ Hz, 1C), 23.0 (d, $J_{CP} = 11.6$ Hz, 1C), 9.2 (s, 1C); $^{31}$P NMR (81 MHz, DMSO-$d_6$): $\delta = -16.4$ (s); ESI/MS(+): $m/z = 323.1675$, calcd. for $[C_{20}H_{24}N_2P]^+$: 323.1672.

**1-[11-(Diphenylphosphino)undecyl]-2,3-dimethylimidazolium hexafluorophosphate (PFIL 6):** PFIL **5** was synthesized as outlined for PFIL **2** to obtain a pale yellow oil; yield: 100%. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 7.64$ (d, $J = 2.1$ Hz, 1H), 7.61 (d, $J = 2.1$ Hz, 1H), 7.45–7.31 (m, 10H), 4.08 (t, $J = 7.3$ Hz, 2H), 3.74 (s, 3H), 2.56 (s, 3H), 2.05 (t, $J = 7.5$ Hz, 2H), 1.75–1.60 (m, 2H), 1.48–1.14 (m, 16H); $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.2$ (s, 1C), 138.6 (d, $J_{C,P} = 13.9$ Hz, 1C), 132.4 (d, $J_{C,P} = 18.4$ Hz, 1C), 128.7–128.3 (m, 2C), 122.3 (s, 1C), 120.8 (s, 1C), 47.5 (s, 1C), 34.7 (s, 1C), 30.4 (d, $J_{C,P} = 12.8$ Hz, 1C), 29.2 (s, 1C), 28.9 (m, 3C), 28.6 (s, 1C), 28.5 (s, 1C), 26.7 (d, $J_{C,P} = 11.1$ Hz, 1C), 25.6–25.3 (m, 2C), 9.1 (s, 1C); $^{31}$P NMR (81 MHz, DMSO-$d_6$): $\delta = -16.4$ (s); ESI/MS(+): $m/z = 435.2921$, calcd. for $[C_{28}H_{40}N_2P]^+$: 435.2924.

## Synthesis of Phosphine Selenides

PFIL (0.12 mmol) and excess selenium powder (40 mg) were dissolved in DMSO-$d_6$ (1.0 g) and stirred overnight under an inert environment. The mixture was filtered through celite and analyzed by $^{31}$P NMR.

## Synthesis of Rhenium Complexes

$ReBr(CO)_3(PFIL)_2$ complexes were synthesized by employing an analogous procedure to that reported by Storhoff and Lewis.[26] This method involves the production of $[ReBr(CO)_3(THF)]_2$ by refluxing $ReBr(CO)_5$ in THF, which is subsequently reacted with 2.0 equiv. of the desired PFIL in $CH_2Cl_2$.

**$ReBr(CO)_3$(PFIL 1)$_2$:** $ReBr(CO)_5$ (113 mg, 0.28 mmol) was dissolved in THF (10 mL) and allowed to reflux for 18 h. After the reaction mixture had cooled to room temperature, the solvent was removed under vacuum and the residue dried for 1 h. 1-[3-(Diphenylphosphino)propyl]-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide (344 mg, 0.57 mmol) was dissolved in degassed $CH_2Cl_2$ (10 mL) and added to the residual solids. The solution was refluxed for 4 h. After the reaction mixture had cooled to room temperature, pentane was added until the product precipitated from solution. The white powder was collected, washed with pentane (3×5 mL) and dried under vacuum; yield: 245 mg (56%); mp 84–85 °C. $^1$H NMR (300 MHz, acetone-$d_6$): $\delta = 7.65$–$7.27$ (m, 24H), 4.28 (t, $J = 7.3$ Hz, 4H), 3.91 (s, 6H), 2.65 (dm, $J_{H,P} = 102$ Hz, 4H), 2.65 (s, 6H), 1.68 (dm, $J_{H,P} = 66$ Hz, 4H); $^{13}$C NMR (75.5 MHz, acetone-$d_6$): $\delta = 145.7$ (s, 1C), 133.6 (t, $J_{C,P} = 4.5$ Hz, 1C), 133.4 (t, $J_{C,P} = 4.5$ Hz, 1C), 131.5 (d, $J = 12.1$ Hz, 1C), 129.7 (m, 1C), 123.5 (s, 1C), 122.1 (s, 1C), 49.2 (t, $J_{C,P} = 7.2$ Hz, 1C), 35.6 (s, 1C), 25.6 (s, 1C), 24.2 (t, $J_{C,P} = 14.3$ Hz, 1C), 9.9 (s, 1C); $^{31}$P NMR: (81 MHz, DMSO-$d_6$): $\delta = -8.5$ (s); IR: (ATR): $\nu_{co} = 2029$, 1946, 1901 cm$^{-1}$; ESI/MS(+): $m/z = 497.0958$, calcd. for $[C_{43}H_{48}O_3N_4BrP_2Re]^{2+}$: 497.0952.

**$ReBr(CO)_3$(PFIL 3)$_2$**: $ReBr(CO)_3$(PFIL **3**)$_2$ was synthesized as outlined for $ReBr(CO)_3$(PFIL **1**)$_2$ to obtain an off-white solid; yield: 65%; mp 134–135 °C. $^1$H NMR (300 MHz, acetone-$d_6$): $\delta = 7.75$–$7.26$ (m, 24H), 4.27 (t, $J = 7.3$ Hz, 4H), 3.89 (s, 6H), 2.68 (dm, $J_{H,P} = 84$ Hz, 4H), 2.60 (s, 6H), 1.63 (m, 4H); $^{13}$C NMR (75.5 MHz, acetone-$d_6$): $\delta = 145.6$ (s, 1C), 133.8 (t, $J_{C,P} = 4.5$ Hz, 1C), 133.3 (t, $J_{C,P} = 4.5$ Hz, 1C), 131.4 (d, $J = 14.3$ Hz, 1C), 129.6 (dt, $J_{C,P} = 12.8$, 4.5 Hz, 1C), 123.4 (s, 1C), 122.1 (s, 1C), 48.9 (t, $J_{C,P} = 7.2$ Hz, 1C), 35.5 (s, 1C), 25.5 (s, 1C), 23.5 (t, $J_{C,P} = 13.6$ Hz, 1C), 10.0 (s, 1C); $^{31}$P NMR: (81 MHz, DMSO-$d_6$): $\delta = -7.7$ (s); IR: (ATR) $\nu_{co} = 2028$, 1945, 1900 cm$^{-1}$; ESI/MS(+): $m/z = 497.0957$, calcd. for $[C_{43}H_{48}O_3N_4BrP_2Re]^{2+}$: 497.0952.

**$ReBr(CO)_3$(PFIL 5)$_2$**: $ReBr(CO)_3$(PFIL **5**)$_2$ was synthesized as outlined for $ReBr(CO)_3$(PFIL **1**)$_2$ to obtain a white solid; yield: 48%; mp 186–187 °C. $^1$H NMR (300 MHz, acetone-$d_6$): $\delta = 7.62$–$7.26$ (m, 24H), 4.26 (t, $J = 7.3$ Hz, 4H), 3.90 (s, 6H), 2.65 (dm, $J_{H,P} = 105$ Hz, 4H), 2.63 (s, 6H), 1.67 (dm, $J_{H,P} = 57$ Hz, 4H); $^{13}$C NMR (75.5 MHz, acetone-$d_6$): $\delta = 144.8$ (s, 1C), 132.8 (t, $J_{C,P} = 4.5$ Hz, 1C), 132.4 (t, $J_{C,P} = 4.5$ Hz, 1C), 130.5 (d, $J = 14.3$ Hz, 1C), 128.7 (m, 1C), 122.6 (s, 1C), 121.1 (s, 1C), 48.1 (t, $J_{C,P} = 7.6$ Hz, 1C), 34.6 (s, 1C), 24.6 (s, 1C), 22.9 (t, $J_{C,P} = 13.6$ Hz, 1C), 8.9 (s, 1C); $^{31}$P NMR (81 MHz, acetone-$d_6$): $\delta = -8.2$ (s); IR (ATR) $\nu_{co} = 2022$, 1935, 1912 cm$^{-1}$; ESI/MS(+): $m/z = 497.0955$, calcd. for $[C_{43}H_{48}O_3N_4BrP_2Re]^{2+}$: 497.0952.

**$ReBr(CO)_3$(PFIL 6)$_2$**: $ReBr(CO)_3$(PFIL **6**)$_2$ was synthesized as outlined for $ReBr(CO)_3$(PFIL **1**)$_2$ to obtain a white solid; yield: 38%; mp 124–125 °C. $^1$H NMR (300 MHz, $CD_3CN$): $\delta = 7.54$–$7.31$ (m, 20H), 7.27–7.19 (m, 4H), 4.00 (t, $J = 7.5$ Hz, 4H), 3.68 (s, 6H), 2.48 (s, 6H), 2.25 (dm, $J_{H,P} = 186$ Hz, 4H), 1.73 (m, 4H), 1.42–0.87 (m, 32H); $^{13}$C NMR

(75.5 MHz, $CD_3CN$): $\delta = 145.4$ (s, 1C), 134.1 (t, $J_{C,P} = 4.5$ Hz, 1C), 133.8 (t, $J_{C,P} = 4.5$ Hz, 1C), 131.3 (d, $J = 7.6$ Hz, 1C), 129.4 (dt, $J_{C,P} = 12.8$, 4.5 Hz, 1C), 123.2 (s, 1C), 121.8 (s, 1C), 49.2 (s, 1C), 35.8 (s, 1C), 31.3 (t, $J_{C,P} = 6.0$ Hz, 1C), 30.3 (s, 1C), 30.1 (s, 2C), 29.9 (s, 1C), 29.7 (s, 1C), 29.6 (s, 1C), 27.2 (t, $J_{C,P} = 13.6$ Hz, 1C), 26.8 (s, 1C), 24.7 (s, 1C), 10.1 (s, 1C); $^{31}P$ NMR (81 MHz, DMSO-$d_6$): $\delta = -8.5$ (s); IR (ATR): $\nu_{co} = 2023$, 1938, 1897 $cm^{-1}$; ESI/MS(+): $m/z =$ 609.2208, calcd. for $[C_{59}H_{80}O_3N_4BrP_2Re]^{2+}$: 609.2204.

### Synthesis of Palladium Nanoparticles

In a typical experiment, $Pd(acac)_2$ (30 mg, 0.10 mmol), PFIL **1–6** (0.10 mmol) and [BDMI]X (2 mL) (BDMI = 1-butyl-2,3-dimethylimidazolium; $X^- = Tf_2N^-$, $TfO^-$, $PF_6^-$) were combined in a glovebox and placed in a high-pressure reactor. After stirring the mixture at 80 °C under an atmosphere of argon for 45 min, a constant pressure of $H_{2(g)}$ (4 bar) was admitted to the system and and the content was stirred for 4 h at 80 °C. The Pd NPs embedded in ionic liquid were employed for hydrogenation studies and TEM analysis. Isolation of the Pd NPs for XPS analysis was achieved by dissolving the mixture in acetone (10 mL), centrifuging (7500 rpm for 10 min), washing with acetone:pentane (2:1) (2 × 10 mL) and drying under vacuum.

### Hydrogenation Studies

In a typical experiment, the synthesized Pd NPs embedded in [BDMI]X were placed in a high-pressure reactor with styrene (2.9 mL, 25 mmol). After evacuating and backfilling the vessel, the mixture was stirred at 50 °C for 1.5 h under a constant pressure of $H_{2(g)}$ (4 bar). The mixture was cooled to room temperature and extracted with pentane (3 × 8 mL). The organic phase was analyzed by gas chromatography employing dodecane as an internal standard and the IL phase was dried under vacuum for at least 1 h. Recycling experiments were performed with the dried IL phase under the reaction conditions outline above. The IL phase was stored under vacuum between catalytic cycles.

### Carbon Disulfide Poisoning Tests

Catalyst poisoning tests employing $CS_2$ were performed as a typical hydrogenation experiment with the addition of $CS_2$ (0.05 mmol, 0.5 equiv.) to the IL:styrene mixture prior to start of the experiment.

### Transmission Electron Microscopy

TEM images of Pd NPs were obtained on a Philips CM 200 microscope operating at an accelerating voltage of 200 kV with a point resolution of 0.24 nm. Sample preparation included dilution of 3 drops of the Pd NP solution in ~1.5 mL of MeCN, followed by deposition on a carbon-coated copper grid (400 mesh) at room temperature. The NP size distribution was determined from the measurement of > 100 spherical particles chosen in arbitrary areas of enlarged micrographs.

### Supporting Information

The Supporting Information contains additional catalytic hydrogenation, TEM, XPS and NMR data for PFIL-stabilized Pd NPs, NMR data for PFIL phosphine selenides, NMR and HR-MS data for the synthesis of PFILs.

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