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PAPER

Rhodium complexes stabilized by phosphine-functionalized phosphonium ionic liquids used as higher alkene hydroformylation catalysts: influence of the phosphonium headgroup on catalytic activity†‡

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Monodentate phosphine-functionalized phosphonium ionic liquids (PFILs) were employed as ligands for Rh complexes and used in the hydroformylation of higher alkenes. Three PFILs were designed by varying the length of the P-alkyl chain attached to the phosphonium moiety, for alkyl = methyl (**1**), butyl (**2**), octyl (**3**), in order to tune their solubility properties. In all PFILs, the phosphonium unit is linked to a diphenylphosphino functionality by an undecyl linker, with bis(trifluoromethylsulfonyl)imide as counter anion. These PFILs were combined with a Rh(I) precursor, [Rh(acac)(CO)$_2$], to provide a biphasic hydroformylation catalyst for the transformation of 1-octene, 1-decene and 1-dodecene using tetradecyltributylphosphonium bis(trifluoromethylsulfonyl)imide, [$P_{4,4,4,14}$]NTf_2 as a solvent. Good activities and excellent selectivities were obtained for these PFILs-Rh(I) complexes. Variation of the P-alkyl length in the PFIL ligand influenced the stability, catalytic activity and selectivity of the PFIL-stabilized catalyst.

Introduction

The Ruhrchemie/Rhône-Poulenc biphasic process represents one of the most important homogeneously catalyzed reactions in the chemical industry.[1,2] The hydroformylation of propene is catalyzed using a water-soluble Rh catalyst stabilized by triphenylphosphine trisulfonate (TPPTS). The Rh catalyst is retained in the aqueous phase, which allows for facile removal of the product and reuse of the catalyst.[1,3] However, this process is less successful for the conversion of long-chain olefins due to their poor solubilities in the aqueous catalytic phase.[3] Long chain linear aldehyde are of major commercial importance and thus various solutions have been explored to increase the reaction rates of higher alkene hydroformylation including: (i) co-solvents;[4–6] (ii) addition of surfactants;[7–15] (iii) amphiphilic phosphines;[16–20] (iv) functionalized cyclodextrins;[21–27] and (v) alternative solvents, such as supercritical CO_2 [28–35] and ionic liquids (ILs).[36–40]

Knifton was the first to report an IL-based hydroformylation catalyst composed of a Ru and/or a Co carbonyl precursor dissolved in a phosphonium IL.[39] Karodia *et al.* also reported the use of phosphonium ILs as solvents for hydroformylation, in which the nature of the phosphonium substitution was shown to have a dramatic influence on the activity and selectivity of the catalyst.[38] Olivier-Bourbigou and co-workers were the first to report the use of imidazolium ILs for hydroformylation.[36,37] Their initial study evidenced leaching of the Rh catalyst from the IL phase in the absence of an additional stabilizing ligand, such as TPPTS.[36] TPPTS allowed for complete retention of the catalyst in the IL phase; however, the activity of the catalyst was dramatically reduced.[36]

In order to improve catalyst retention and stabilization in IL biphasic systems, homogeneous catalysts have been stabilized by functionalized ILs (FILs) – ILs featuring a metal binding functionality.[36,37,41–47] Several groups have reported phosphine and phosphite based FILs as hydroformylation ligands that improve the solubility of higher alkene reactants in the catalytic phase, while simultaneously improving catalyst retention and selectivity.[33,35,42,45,46,48–54]

In the context of IL-stabilized transition metal nanoparticles (NPs),[55–65] our group and others have studied the influence of changing the parameters of FILs (*i.e.* alkyl chain length, counter anion) on the catalytic properties of transition metal NPs.[57,66–68] FILs represent a highly tunable class of ligands, in which systematic alterations to the FIL structure can be accomplished to understand their influence on the stability, activity and selectivity of a catalyst. For example, a series of imidazolium ILs functionalized with a phosphine[66,67] or a bipyridine[68] moiety were designed such that the alkyl linker between the cationic and metal binding functionalities was used to tune catalytic activity of transition metal NPs. Herein, we have applied this concept to the design of new phosphine-functionalized ILs (PFILs) in order

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† Dedicated to David Cole-Hamilton, a patient supervisor, a passionate mentor.

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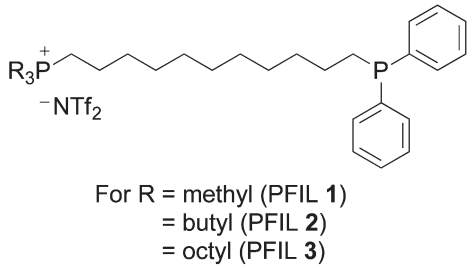

Fig. 1 Phosphine-functionalized phosphonium ionic liquids (PFILs) **1–3** used as ligands for the hydroformylation of long-chain alkenes.

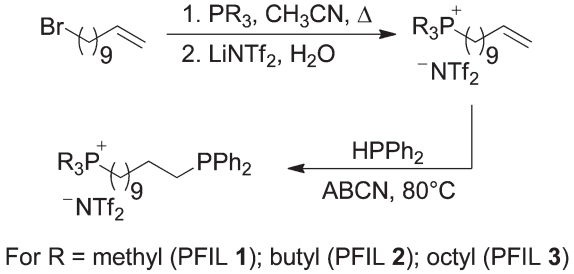

Fig. 2 Synthesis of PFILs **1–3**.

to better understand the impact of the PFIL on directing the activity and selectivity in Rh(I) catalyzed hydroformylation.

The novel PFILs **1–3** (Fig. 1) were synthesized, in which the P-alkyl chain length was varied, with R = methyl (**1**), butyl (**2**), octyl (**3**). The coordination properties of these new ligands to Rh(I) species was studied by ^{31}P NMR. These PFILs were also used as stabilizing ligands for Rh(I) complexes employed in the biphasic hydroformylation of higher alkenes in a phosphonium IL solvent, $[P_{4,4,4,14}]NTf_2$ ($P_{4,4,4,14}$ = tetradecyltributylphosphonium, $^{-}NTf_2$ = bis(trifluoromethylsulfonyl)imide). Phosphonium ILs impart several advantages to this system: (1) high chemical and thermal stability;[69] (2) lower cost alternatives to imidazolium ILs;[70] and (3) possess higher gas diffusivity than imidazolium ILs of equal viscosity.[60] Furthermore, the long chain alkyl groups of the PFILs and the IL solvent could increase the solubility of the alkene substrate in the IL phase and facilitate the interaction of the substrate with the active metal sites. The diphenylphosphino moiety of PFILs **1–3** was shown by NMR to have similar electronic features upon coordination to a Rh(I) centre, allowing to probe solely the steric and solubility properties. The activities and selectivities of the PFIL-stabilized Rh catalysts in the hydroformylation of 1-octene, 1-decene and 1-dodecene were dependent on the nature of the phosphonium headgroup. In general, the longer chain PFIL possessed superior activities, while the shorter chain PFILs provided improved selectivities.

Results and discussion

(a) Synthesis of phosphine-functionalized ionic liquids

The synthesis of PFILs **1–3** followed a similar procedure to that reported previously by our group for the synthesis of imidazolium PFILs.[66] The procedure involved a radical chain addition of diphenylphosphine to alkene-functionalized ILs catalyzed by 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) to introduce the desired phosphines in almost quantitative yields (Fig. 2). Undecenyl phosphonium salts were synthesized through the quaternization of the desired phosphine (R = methyl, butyl, octyl) with undecenyl bromide, followed by an anion exchange using $LiNTf_2$.

(b) NMR study of the Rh(I) complexes of PFILs 1–3

Monodentate phosphines are known to form with Rh(I) a variety of coordination species under hydroformylation conditions. The

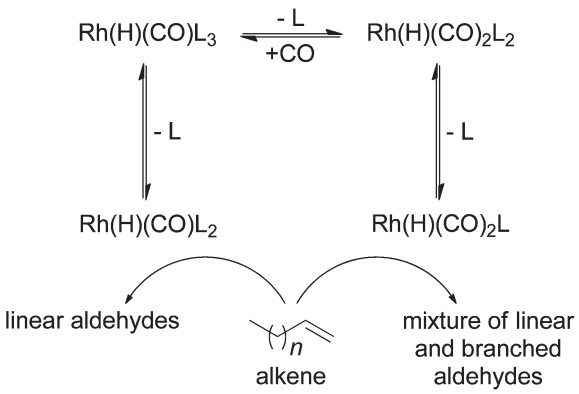

Fig. 3 Precatalytic hydroformylation complexes stabilized by a monodentate phosphine (L) responsible for the regioselectivity of the aldehyde products.

nature of the catalytic complex has a crucial impact on both the catalyst activity, and the selectivity towards the desired linear aldehyde over the branched one, as described in Fig. 3.[2] Phosphine disassociation leads to two unsaturated intermediates, $Rh(H)(CO)L_2$ and $Rh(H)(CO)_2L$, which are responsible for the formation of the aldehyde product. The bisphosphine species $Rh(H)(CO)L_2$ selectively produces the least hindered product, the linear aldehyde, while $Rh(H)(CO)_2L$ yields both the linear and branched product.[2,71] Therefore, the hydroformylation regioselectivity can be tuned by controlling the concentration of $Rh(H)(CO)L_2$.

Recently Klein Gebbink and co-workers used ^{31}P NMR spectroscopy to demonstrate that charged phosphines were behaving differently than neutral ones in respect to coordination to Rh(I) species.[71] A similar NMR experiment was performed to gain insight into the coordination properties of PFIL **1–3** (Table 1). To the precursor $[Rh(COD)_2][OTf]$, 1 to 4 equivalents of PFIL **1–3** were added in d^3-acetonitrile as solvent (COD = cyclooctadiene).

Stirring one equivalent of PFIL **1–3** with $[Rh(COD)_2][OTf]$ at room temperature rapidly afforded the expected 1 : 1 complex characterized by a doublet in ^{31}P NMR (Fig. 4, Table 1, entries 4–6). Addition of a second equivalent gave rise to two signals, a doublet of doublets and a doublet of triplets, which are characteristic of a tri-phosphine-substituted rhodium species. This set of signals correspond to an A_2BX system, consistent with square planar $[Rh(MeCN)(PFIL)_3][OTf]$. No other peak was observed – no free PFIL or mono-phosphine-substituted complex – but the

base line was noisy: exchange is expected to happen between these three species. The addition of a third equivalent of PFIL confirms the full formation of the [Rh(MeCN)(PFIL)$_3$][OTf] complex (Fig. 4, Table 1, entries 7–9). Absence of coordinated COD is also confirmed by ^{1}H NMR. Addition of more PFIL led to the appearance of a signal of free PFIL, confirming that 3 is the maximum PFIL/Rh ratio for these species. PFILs **1–3** all behaved in the same fashion. The chemical shifts of the PPh_2 signals of [Rh(MeCN)(PFIL)$_3$][OTf] complexes for PFIL **1–3** ranged from δ = 35.2 to 35.5 ppm (dt) and δ = 22.4 to 22.5 ppm (dd) with coupling constants of $^1J_{Rh-P}$ = 172 to 173 (dt) and 133 Hz (dd). These values are very similar and prove that PFILs **1–3** have essentially the same electronic behaviour towards Rh(I). These properties are also close to those observed when PPh_3 is used as the ligand under the same conditions (δ = 45.5 ppm, $^1J_{Rh-P}$ = 174 Hz (dt), δ = 32.8 ppm, $^1J_{Rh-P}$ = 137 Hz (dd)).[71]

(c) Hydroformylation catalysis

Hydroformylation tests were performed on long-chain alkene substrates in [$P_{4,4,4,14}$]NTf_2 ($P_{4,4,4,14}$ = tetradecyltributylphosphonium) as solvent in the presence of [Rh(acac)(CO)$_2$] (acac = acetylacetonate) as pre-catalyst and a PFIL ligand (Fig. 5). Initial studies employed PFIL **1** for the hydroformylation of 1-octene to optimize various reaction parameters. The PFIL **1**/Rh ratio influenced both the conversion and selectivity of this reaction (Table 2, entries 1–4). The conversion of 1-octene was >98% for 2, 4 and 8 eq. of PFIL **1**, while the conversion was decreased to 88% with 12 eq. of the phosphine ligand. Further, the linear-to-branched (*l*/*b*) ratio for the aldehyde product increased with an increase in the amount of PFIL **1** added to the reaction mixture. A PFIL **1**/Rh ratio of 8 was employed for further studies since these conditions were a

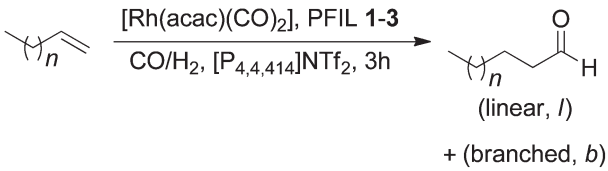

Fig. 5 Biphasic hydroformylation of higher alkenes catalyzed by [Rh(acac)(CO)$_2$] and PFILs **1–3** (for n = 5, 7, 9).

Table 1 ^{31}P NMR spectral data for the PFIL **1–3** and a series of PFIL **1–3**: Rh(I) complexes

Entry	^{31}P species	δ_{PR3+} (ppm)	δ_{PPh2} (ppm)	$^1J_{P-Rh}$ (Hz)	$^2J_{P-P}$ (Hz)
1	PFIL **1**	26.8	−17.0	—	—
2	PFIL **2**	33.7	−17.0	—	—
3	PFIL **3**	33.6	−17.0	—	—
4	[Rh(COD)(MeCN)(**1**)]$^+$	26.9	23.0	143	—
5	[Rh(COD)(MeCN)(**2**)]$^+$	33.6	23.0	143	—
6	[Rh(COD)(MeCN)(**3**)]$^+$	33.6	23.0	143	—
7	[Rh(MeCN)(**1**)$_3$]$^+$	26.9	35.4(dt)	173	42
			22.4(dd)	133	42
8	[Rh(MeCN)(**2**)$_3$]$^+$	33.6	35.2(dt)	172	43
			22.5(dd)	133	42
9	[Rh(MeCN)(**3**)$_3$]$^+$	33.6	35.5(dt)	173	43
			22.5(dd)	133	43

Reaction conditions: [Rh(COD)$_2$][OTf] = 0.05 mmol, PFIL/Rh = 1 or 3, T = RT, t = 30 min. Note: in all Rh : PFIL complexes, the counter anion is $^-$OTf.

Table 2 Optimization of the reaction conditions for the biphasic hydroformylation of 1-octene catalyzed by [Rh(acac)(CO)$_2$] and PFIL **1**

Entry	PFIL **1**/Rh	T (°C)	p[CO/H$_2$] (bar)	Conversion[a] (%)	l/b[b]	S_{ad}[c] (%)
1	2	100	40	100	1.8	88
2	4	100	40	98	2.3	86
3	8	100	40	98	2.2	85
4	12	100	40	88	2.8	84
5	8	75	40	91	2.8	95
6	8	50	40	28	3.0	100
7	8	75	20	91	3.7	100
8	8	75	10	57	3.6	88

Reaction conditions: [Rh(acac)(CO)$_2$] = 0.05 mmol, [$P_{4,4,4,14}$]NTf_2 = 1.0 g, 1-octene/Rh = 100, CO/H$_2$ = 1/1, t = 3 h. [a] Determined by GC analysis employing dodecane as an internal standard. [b] Ratio linear/branched aldehyde. [c] S_{ad} = aldehyde selectivity (percentage [linear + branched aldehydes]/[total conversion]).

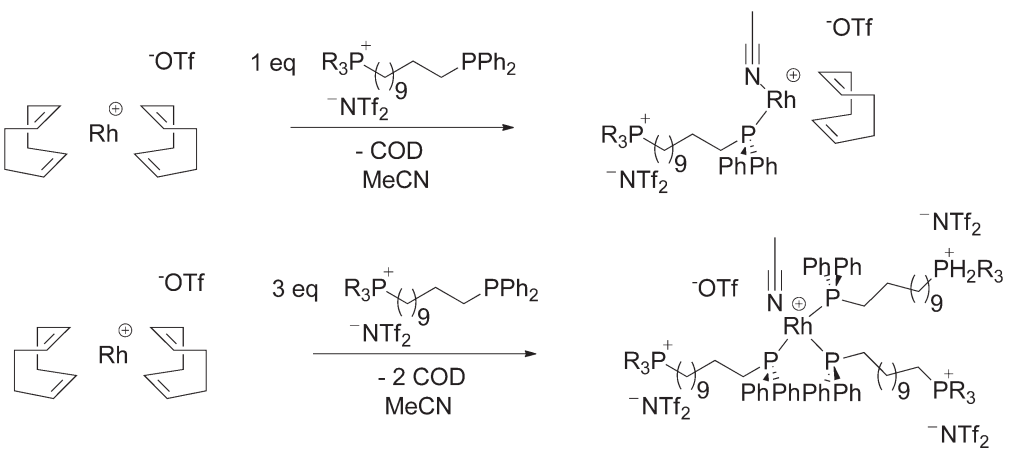

Fig. 4 Coordination behaviour of PFIL **1–3** with [Rh(COD)$_2$][OTf]. For R = methyl (PFIL **1**); butyl (PFIL **2**); octyl (PFIL **3**).

Table 3 Influence of PFIL structure on the biphasic hydroformylation of higher alkenes catalyzed by [Rh(acac)(CO)$_2$] and PFILs **1–3**

Entry	PFIL	Substrate	Conversion[a] (%)	*l*/*b*[b]	S_{ad}[c] (%)
1	**1**	1-Octene	64	3.0	97
2	**2**	1-Octene	60	2.8	98
3	**3**	1-Octene	94	2.8	100
4	**1**	1-Decene	58	3.3	97
5	**2**	1-Decene	55	2.9	96
6	**3**	1-Decene	66	2.9	92
7	**1**	1-Dodecene	53[d]	2.9	97
8	**2**	1-Dodecene	45[d]	3.3	98
9	**3**	1-Dodecene	70[d]	2.8	93

Reaction conditions: [Rh(acac)(CO)$_2$] = 0.05 mmol, PFIL/Rh = 8, [$P_{4,4,4,14}$]NTf_2 = 1.0 g, alkene/Rh = 250, CO/H_2 = 1/1 (20 bar), T = 75 °C, t = 3 h. [a] Determined by GC analysis employing dodecane as an internal standard. [b] Ratio linear/branched aldehyde. [c] S_{ad} = aldehyde selectivity (percentage [linear + branched aldehydes]/[total conversion]). [d] Decane used as an internal standard.

Table 4 Catalyst recycling for the biphasic hydroformylation of 1-octene catalyzed by [Rh(acac)(CO)$_2$] and PFILs **1–3**

Entry	Ligand	Cycle	Conversion[a] (%)	*l*/*b*[b]	S_{ad}[c] (%)
1	PFIL **1**	1	91	3.7	100
2		2	95	3.6	100
3		3	94	3.3	100
4		4	56	3.2	100
5		5	61	3.1	100
6	PFIL **2**	1	95	4.1	82
7		2	96	3.6	91
8		3	92	3.7	96
9		4	88	3.4	97
10		5	84	3.2	97
11	PFIL **3**	1	81	3.4	100
12		2	81	3.4	100
13		3	84	3.2	100
14		4	85	3.2	100
15		5	87	3.1	100
16	PPh_3	1	99	3.9	93
17		2	91	2.8	93
18		3	89	2.5	94
19		4	90	2.4	94
20		5	74	2.4	90

Reaction conditions: [Rh(acac)(CO)$_2$] = 0.05 mmol, PFIL/Rh = 8, [$P_{4,4,4,14}$]NTf_2 = 1.0 g, 1-octene/Rh = 100, CO/H_2 = 1/1 (20 bar), T = 75 °C, t = 3 h. [a] Determined by GC analysis employing dodecane as an internal standard. [b] Ratio linear/branched aldehyde. [c] S_{ad} = aldehyde selectivity (percentage [linear + branched aldehydes]/[total conversion]).

compromise between stability, activity and selectivity. Decreasing the reaction temperature from 100 to 75 or 50 °C increased the *l*/*b* ratio of the product mixture (Table 2, entries 1, 5, 6). A reaction temperature of 75 °C was favoured as the 1-octene conversion remained high, while the *l*/*b* ratio was increased from 2.2 at 100 °C to 2.8 at 75 °C. Lastly, a further increase in the *l*/*b* ratio was obtained by altering the syngas pressure (Table 2, entries 1, 7, 8). Decreasing the reaction pressure from 40 to 20 bar improved the *l*/*b* ratio to 3.7, an excellent selectivity for a monodentate ligand. A further pressure decrease to 10 bar negatively impacted the 1-octene conversion.

These optimized catalytic conditions were employed to study the influence of the PFIL stabilizer and the substrate in this reaction. For this study the alkene/Rh ratio was increased to 250 eq. while all other reaction conditions were held constant. For 1-octene, PFILs **1** and **2** possessed similar activities and selectivities (Table 3, entries 1 and 2), while the activity of the PFIL **3**-stabilized catalyst reached 94% conversion (Table 3, entry 3). PFILs **1–3** also provided active catalysts for the hydroformylation of 1-decene and 1-dodecene. PFIL **1** and **2** showed moderate activities for 1-decene and 1-dodecene (Table 3, entries 4, 5, 7, 8). Again PFIL **3** provided the most active catalyst for 1-decene and 1-dodecene (Table 3, entries 6 and 9) achieving an alkene conversion of ~70% for both substrates, while maintaining similar *l*/*b* selectivities. With both 1-octene and 1-decene, the best selectivities were obtained for the short alkyl chain PFIL **1** (Table 3, entries 1 and 4), with a value up to 3.3, which is high for a monodendate phosphine.[71] The ^{31}P NMR study did not indicate significant impact of the higher steric hindrance of **2–3** on their coordination behaviour in acetonitrile. However, in the phosphonium ionic liquid medium of catalysis, the difference in *l*/*b* selectivities is a clear indication that the PFIL **1** may favour Rh(H)(CO)(PFIL)$_2$ over Rh(H)(CO)$_2$(PFIL) more efficiently than the bulkier PFILs **2** and **3**. As both the charge and the electronic properties of the ligands PFIL **1–3** are essentially identical, these results demonstrate the impact of sterics and the lipophilic character of the stabilizing species in homogeneous catalysis.

The recyclability of the PFIL-stabilized catalysts was investigated for the hydroformylation of 1-octene with a substrate/catalyst ratio of 100 (Table 4). Rh catalysts were prepared *in situ* from the combination of [Rh(acac)(CO)$_2$] and PFILs **1–3** in [$P_{4,4,4,14}$]NTf_2. After catalysis, the product was extracted using pentane and the recovered IL was dried *in vacuo* for 1 h. The catalyst phase was recharged with substrate for a subsequent catalytic cycle and employed for a total of five hydroformylation cycles. As outlined in Table 4, the alkene conversion, *l*/*b* ratio and aldehyde selectivity were dependent on the nature of the PFIL stabilizer. PFILs **2** and **3** provided the most active catalysts able to maintain a 1-octene conversion >84% over five catalytic cycles. The stability of the catalyst based on PFIL **1** was reduced compared to **2** and **3** as a significant decrease in 1-octene conversion occurred after the third cycle. In terms of the *l*/*b* ratio, PFILs **1** and **2** initially possessed *l*/*b* ratios of 3.7 and 4.1 respectively, which both decreased to 3.1 by the fifth cycle. PFIL **3** initially had a lower *l*/*b* ratio of 3.4; however, this catalyst did not suffer from a significant decrease of the *l*/*b* ratio over the five cycles. Lastly, PFILs **1** and **3** showed quantitative conversion of 1-octene to aldehyde products, whereas PFIL **2** catalyzed the isomerization of octene more readily as reflected in the S_{ad}.

PPh_3 was also employed as a stabilizer to compare a neutral phosphine to PFILs **1–3** (Table 4, entries 16–20). The catalytic activity of the PPh_3-stabilized catalyst was >90% over the first four cycles; however, the conversion decreased during the fifth cycle (74%). The *l*/*b* ratio also decreased upon recycling from 3.9 during the first cycle to 2.4 during the fifth cycle. Isomerization of 1-octene was more readily catalyzed in this system as the S_{ad} was <94%. The stability of the PPh_3 catalyst was reduced compared to that of the PFILs. Qualitatively, the IL phase transformed from a bright orange solution to a dark brown suspension after the second catalytic cycle, signifying the formation of Rh(0) NPs.[72]

A transmission electron microscopy (TEM) study was undertaken to better understand the nature of the catalyst for each PFIL **1**/Rh ratio after catalysis (Fig. S1, see ESI‡ for additional TEM data). Small Rh(0) NPs with diameters ~2 nm were formed for PFIL **1**/Rh ratios higher than 8; however, ratios lower than 8 resulted in the formation of a mixture of heterodispersed particles of sizes ranging from 2 to several hundreds of nm. The catalysis data proved that 8 eq. of PFIL was also required to form a selective catalyst by favouring the formation of the bisphosphine complex and to enhance the stability of the Rh(I) catalyst under catalytic conditions. TEM analysis of the IL phase with each PFIL and PPh_3 was also obtained after five cycles of catalysis and showed the presence of NPs ranging from ~2–10 nm (Fig. S2‡). The NP size and concentration was dependent on the nature of the phosphine stabilizer. PFILs **1** and **2** provided the most stable catalysts as only a low concentration of ~2 nm NPs were observed, while PFIL **3** showed the presence of NPs ranging from ~2–10 nm. The PPh_3-stabilized catalyst showed a higher concentration of NPs compared to PFILs **1–3** and could result from the insolubility of PPh_3 in the IL solution.[67] Further, the PPh_3 catalyst solution turned from an orange to a dark brown colour, signifying the formation of a high concentration of Rh NPs,[72] while the solutions containing PFILs **1–3** remained orange throughout the recycling experiments. It should be noted that Dupont and co-workers have employed Rh(0) NPs synthesized in imidazolium ILs as hydroformylation catalyst precursors.[72] These Rh NPs acted as a reservoir for the formation of catalytically active Rh(I) mononuclear complexes; however, possessed low *l*/*b* ratios for the aldehyde products in the absence of an additional stabilizing ligand.[72] In our system, Rh NPs were also formed, but unlike the results reported by Dupont, the inclusion of these PFIL ligands allowed the catalyst system to maintain high *l*/*b* ratios. It is reasonable to assume that our NPs may also act as a reservoir in the formation of Rh(I) monomeric complexes, while the PFIL effectively coordinates Rh(I) species to afford excellent selectivity. In order to test the catalytic properties of the Rh NPs themselves, an experiment was performed where Rh NPs were created in the presence of PFIL **2** *in situ* before addition of 1-octene. In this test, the *l*/*b* ratio dropped to 1.8, while the conversion (78.4%) and aldehyde selectivity (94%) was also adversely affected. This is consistent with the idea that Rh NPs may serve as a source of Rh, but that they do not explain the catalysis itself.[71]

Conclusions

Phosphine-functionalized phosphonium ILs **1–3**, possessing variable P-alkyl chain lengths, were effective stabilizing species in the preparation of higher alkene hydroformylation catalysts. The nature of the PFIL phosphonium headgroup influenced the coordination modes, stability, catalytic activity, selectivity and recyclability of the corresponding Rh catalysts. Long alkyl chains on the phosphonium headgroup favoured conversion by improving high alkene solubility, while short chains favoured selectivity by maintaining a higher concentration of the bisphosphine Rh(I) complex. PFILs were also compared to PPh_3 and were shown to improve the catalytic activity and selectivity of the hydroformylation catalyst. Future studies will include the design of bidentate phosphine functionalized ILs for catalysis.

Experimental

(a) General

All syntheses were carried out under an argon atmosphere employing Schlenk techniques. Tetradecylmethanesulfonate,[73] $[P_{4,4,4,14}]OMs$[65] and $[P_{4,4,4,14}]NTf_2$ [65] was prepared following a known literature procedure. Dichloromethane (Grubbs apparatus) and triethylamine (distillation over CaH_2) were purified prior to use. All other chemicals and solvents were purchased from commercial sources and used without further purification. 1-Octene, 1-decene and 1-dodecene were degassed prior to use and storage under an inert atmosphere. Melting points (mp) were determined on a Gallenkamp melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a 200 or 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 LTQ Orbitrap ESI/APCI (Thermo Scientific). Transmission electron microscopy (TEM) was performed on a Phillips CM 200 microscope. High-pressure experiments were performed employing a Parr Instruments 5000 Series Multiple Reactor System equipped with 100 mL reaction vessels. Gas chromatography (GC) was performed on an Agilent 7890A Gas Chromatograph equipped with an Agilent HP-5MS column.

(b) Synthesis of phosphine-functionalized ionic liquids

Synthesis of trialkyl(undec-10-enyl)phosphonium bromide. Trialkylphosphine (23.0 mmol) and 11-bromo-1-undecene (23.0 mmol) were combined in a Schlenk flask and dissolved in CH_3CN (20 mL). The reaction mixture was refluxed for 18 h. The solvent was removed to yield the product, which was washed with pentane (3 × 50 mL) and removed by decantation. The product was dried *in vacuo* overnight at 60 °C.

Trimethyl(undec-10-enyl)phosphonium bromide. The reaction provided an off-white solid (79%). mp 171–173 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.01–4.87 (m, 2H), 2.53–2.36 (m, 2H), 2.19 (d, J = 14.2 Hz, 9H), 2.07–1.89 (m, 2H), 1.62–1.39 (m, 4H), 1.39–1.15 (m, 10H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.3 (s), 114.4 (s), 34.0 (s), 30.7 (d, J_{CP} = 15.6 Hz), 29.5 (s), 29.4 (s), 29.2 (s), 29.2 (s), 29.1 (s), 24.0 (d, J_{CP} = 52.1 Hz), 21.9 (d, J_{CP} = 4.6 Hz), 9.2 (d, J_{CP} = 55.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$) δ 28.1 (s). ESI/MS (+) *m*/*z* calc. for $[C_{14}H_{30}P]^+$ 229.2080, found 229.2086.

Tributyl(undec-10-enyl)phosphonium bromide. The reaction provided a yellow liquid (97%). ^1H NMR (300 MHz, $CDCl_3$) δ 5.60 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 4.91–4.62 (m, 2H), 2.41–2.10 (m, 8H), 1.83 (q, J = 6.8 Hz, 2H), 1.50–1.22 (m, 16H), 1.22–1.01 (m, 10H), 0.78 (t, J = 6.9 Hz, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 138.9 (s), 113.9 (s), 33.5 (s), 30.6 (d, J_{CP} = 14.7 Hz), 29.1 (s), 29.0 (s), 28.8 (s), 28.7 (s), 28.6 (s), 23.9–23.5 (m, 2C), 21.7 (d, J_{CP} = 4.7 Hz), 19.1 (d, J_{CP} = 46.8 Hz), 18.9 (d, J_{CP} = 47.6 Hz), 13.3 (s). ^{31}P NMR (81.0 MHz, $CDCl_3$) δ 33.8 (s). ESI/MS(+) *m*/*z* calc. for $[C_{23}H_{48}P]^+$ 355.3499, found 355.3494.

Trioctyl(undec-10-enyl)phosphonium bromide. The reaction provided a yellow liquid (99%). ^1H NMR (300 MHz, $CDCl_3$) δ

5.66 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.94–4.61 (m, 2H), 2.46–2.15 (m, 8H), 1.90 (q, J = 7.0 Hz, 2H), 1.50–1.05 (m, 50H), 0.74 (t, J = 6.7 Hz, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.0 (s), 114.1 (s), 33.7 (s), 31.6 (s), 30.7 (d, J_{CP} = 14.6 Hz), 29.4–28.7 (m, 10C), 22.5 (s), 21.9 (d, J_{CP} = 4.8 Hz), 19.3 (d, J_{CP} = 46.8 Hz), 14.0 (s). ^{31}P NMR (81 MHz, $CDCl_3$) δ 33.7 (s). ESI/MS(+) m/z calc. for $[C_{35}H_{72}P]^+$ 523.5366, found 523.5372.

Synthesis of trialkyl(undec-10-enyl)phosphonium bis(trifluoromethylsulfonyl) imide. Trialkyl(undec-10-enyl)phosphonium bromide (17.0 mmol) was dissolved in H_2O (50 mL). Bis(trifluoromethanesulfonimide) lithium salt (17.9 mmol) was added in portions and the mixture was stirred vigorously at rt 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 *in vacuo* overnight at 60 °C.

Trimethyl(undec-10-enyl)phosphonium bis(trifluoromethylsulfonyl)imide. The reaction provided an amber liquid (90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H), 5.05–4.80 (m, 2H), 2.18–1.94 (m, 4H), 1.80 (d, J = 14.0 Hz, 9H), 1.61–1.12 (m, 14H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.3 (s), 119.9 (q, J_{CF} = 321.6 Hz), 114.3 (s), 33.9 (s), 30.5 (d, J_{CP} = 16.0 Hz), 29.4 (s), 29.3 (s), 29.2 (s), 29.2 (s), 29.0 (d, J_{CP} = 0.8 Hz), 23.3 (d, J_{CP} = 52.1 Hz), 21.6 (d, J_{CP} = 4.6 Hz), 7.9 (d, J_{CP} = 54.4 Hz). ^{31}P NMR (81 MHz, $CDCl_3$) δ 27.6 (s). ESI/MS(+) m/z calc. for $[C_{14}H_{30}P]^+$ 229.2080, found 229.2085.

Tributyl(undec-10-enyl)phosphonium bis(trifluoromethylsulfonyl)imide. The reaction provided a yellow liquid (92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.04–4.76 (m, 2H), 2.19–1.86 (m, 12H), 1.58–1.18 (m, 24H), 0.92 (t, J = 6.9 Hz, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.1 (s), 119.9 (q, J_{CF} = 321.6 Hz), 114.1 (s), 33.7 (s), 30.5 (d, J_{CP} = 14.7 Hz), 29.4–28.6 (m, 5C), 23.7 (d, J_{CP} = 15.1 Hz), 23.4 (d, J_{CP} = 4.5 Hz), 21.4 (d, J_{CP} = 4.5 Hz), 18.5 (d, J_{CP} = 47.6 Hz), 18.3 (d, J_{CP} = 47.6 Hz), 13.2 (s). ^{31}P NMR (81.0 MHz, $CDCl_3$) δ 34.2 (s). ESI/MS(+) m/z calc. for $[C_{23}H_{48}P]^+$ 355.3488, found 355.3492.

Trioctyl(undec-10-enyl)phosphonium bis(trifluoromethylsulfonyl)imide. The reaction was performed as outlined above expect $CH_3CN : H_2O$ (1 : 1) was employed as the solvent to yield a yellow liquid (91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.01–4.81 (m, 2H), 2.16–1.90 (m, 10H), 1.54–1.18 (m, 50H), 0.84 (t, J = 7.5 Hz, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.3 (s), 120.0 (q, J_{CF} = 321.6 Hz), 114.3 (s), 33.9 (s), 31.8 (s), 30.6 (d, J_{CP} = 14.7 Hz), 29.5–28.8 (m, 10H), 22.7 (s), 21.6 (d, J_{CP} = 4.7 Hz), 18.7 (d, J_{CP} = 46.8 Hz), 14.2 (s). ^{31}P NMR (81 MHz, $CDCl_3$) δ 34.1 (s). ESI/MS(+) m/z calc. for $[C_{35}H_{72}P]^+$ 523.5366, found 523.5361.

Synthesis of (11-(diphenylphosphino)undecyl)trialkyl-phosphonium bis(trifluoromethylsulfonyl)imide (PFIL 1–3). Trialkyl(undec-10-enyl)phosphonium bis(trifluoromethyl-sulfonyl)imide (3.20 mmol), diphenylphosphine (6.40 mmol) and 1,1′-azobis(cyclohexane-carbonitrile) (ABCN) (0.06 mmol) were combined in a Schlenk flask. The mixture was stirred at 80 °C for 72 h, during which time ABCN (0.30 mmol) was recharged twice. The volatiles were removed *in vacuo* and the resulting oil was washed with pentane (3 × 20 mL). The product was dried *in vacuo* overnight at 60 °C.

PFIL 1. The reaction provided a pale yellow liquid (100%). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.45–7.30 (m, 10H), 2.23–1.96 (m, 4H), 1.80 (d, J = 14.8 Hz, 9H), 1.57–1.10 (m, 18H). ^{13}C NMR (75.5 MHz, $(CD_3)_2SO$) δ 138.7 (d, J_{CP} = 13.9 Hz), 132.3 (d, J_{CP} = 18.9 Hz), 128.5 (m, 2C), 119.5 (q, J_{CF} = 322.4 Hz), 30.4 (d, J_{CP} = 12.1 Hz), 30.0 (d, J_{CP} = 15.9 Hz), 28.9 (s), 28.8 (s), 28.7 (s), 28.7 (s), 28.3 (s), 26.7 (d, J_{CP} = 10.6 Hz), 25.5 (d, J_{CP} = 15.9 Hz), 22.2 (d, J_{CP} = 52.1 Hz), 20.5 (d, J_{CP} = 3.8 Hz), 7.1 (d, J_{CP} = 53.6 Hz). ^{31}P NMR (81 MHz, $(CD_3)_2SO$) δ 29.0 (s), −16.4 (s). ESI/MS(+) m/z calc. for $[C_{26}H_{41}P_2]^+$ 415.2678, found 415.2687.

PFIL 2. The reaction provided a pale yellow liquid (100%). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.44–7.31 (m, 10H), 2.25–2.10 (m, 8H), 2.04 (t, J = 7.5 Hz, 2H), 1.54–1.14 (m, 30H), 0.91 (t, J = 7.0 Hz, 9H). ^{13}C NMR (75.5 MHz, $(CD_3)_2SO$) δ 138.6 (d, J_{CP} = 14.0 Hz), 132.3 (d, J_{CP} = 18.1 Hz), 128.5 (s), 128.4 (s), 119.5 (q, J_{CF} = 322.4 Hz), 30.3 (d, J_{CP} = 12.1 Hz), 30.0 (d, J_{CP} = 15.1 Hz), 28.8 (d, J_{CP} = 2.3 Hz), 28.6 (s), 28.1 (s), 26.7 (d, J_{CP} = 11.1 Hz), 25.5 (d, J_{CP} = 15.9 Hz), 23.3 (d, J_{CP} = 15.6 Hz), 22.6 (d, J_{CP} = 4.4 Hz), 20.5 (d, J_{CP} = 4.3 Hz), 17.8 (s), 17.6 (s), 17.1 (s), 17.0 (s), 13.2 (s). ^{31}P NMR (81 MHz, $(CD_3)_2SO$) δ 34.9 (s), −16.3 (s). ESI/MS(+) m/z calc. for $[C_{35}H_{59}P_2]^+$ 541.4087, found 541.4085.

PFIL 3. The reaction provided a pale yellow liquid (87%). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.43–7.28 (m, 10H), 2.24–2.08 (m, 8H), 2.04 (t, J = 7.5 Hz, 2H), 1.55–1.15 (m, J = 54H), 0.85 (t, J = 7.6 Hz, 9H). ^{13}C NMR (75.5 MHz, $(CD_3)_2SO$) δ 138.6 (d, J_{CP} = 14.0 Hz), 132.3 (d, J_{CP} = 18.4 Hz), 128.5–128.3 (m, 2C), 119.5 (q, J_{CF} = 322.4 Hz), 31.2 (s), 30.4 (d, J_{CP} = 12.8 Hz), 30.2–29.8 (m, 2C), 29.0–28.0 (m, 9C), 26.8 (d, J = 11.3 Hz), 25.5 (d, J = 16.0 Hz), 22.1 (s), 20.5 (d, J = 4.2 Hz), 17.4 (d, J_{CP} = 47.6 Hz), 13.8 (s). ^{31}P NMR (81.0 MHz, $(CD_3)_2SO$) δ 34.9 (s), −16.3 (s). ESI/MS(+) m/z calc. for $[C_{47}H_{83}P_2]^+$ 709.5965, found 709.5989.

(c) Synthesis of phosphonium ionic liquids

Synthesis of $[P_{4,4,4,14}]NTf_2$ was previously reported by Del Sesto *et al.* and involved the quaternization of tributylphosphine with 1-chlorotetradecane, followed by a salt metathesis with $LiNTf_2$.[74] To avoid possible halide contamination,[75] $[P_{4,4,4,14}]NTf_2$ was synthesized from the quaternization of tetradecylmethanesulfonate with tributylphosphine to form tetradecyltributylphosphonium methanesulfonate, $[P_{4,4,4,14}]OMs$. The intermediate $[P_{4,4,4,14}]OMs$ salt was subjected to an anion exchange with $LiNTf_2$ to yield tetradecyltributylphosphonium bis(trifluoromethylsulfonyl)imide, $[P_{4,4,4,14}]NTf_2$. The experimental procedure for the synthesis of $[P_{4,4,4,14}]NTf_2$ has been previously reported by our group.[65]

(d) ^{31}P NMR study

$[Rh(COD)_2][OTf]$ (0.05 mmol), PFIL (1, 2, 3 or 4 eq.) and CD_3CN (1.0 g) were combined and stirred at room temperature for 30 min. 10 mg of $OPOct_3$ was used as internal standard. ^{31}P NMR and ^{1}H NMR were recorded.

(e) Procedure for hydroformylation

[Rh(acac)(CO)$_2$] (0.05 mmol), PFIL, alkene, and [$P_{4,4,4,14}$]NTf_2 (1.0 g) were combined and stirred at 50 °C for 15 min. After evacuating and backfilling the vessel, the mixture was stirred at 100 °C for 3 h under a constant pressure of CO/H_2 (1/1). The mixture was cooled to rt and extracted with pentane (3 × 7 mL). The organic phase was analyzed by gas chromatography employing dodecane as an internal standard for 1-octene and 1-decene, while decane was employed as an internal standard for 1-dodecene. Recycling experiments were performed once the IL phase was dried *in vacuo* for at least 1 h under the reaction conditions outline above. The IL phase was stored under an inert atmosphere between catalytic cycles.

(f) Transmission electron microscopy

TEM of the IL phase was obtained on a Phillips CM 200 microscope operating at an accelerating voltage of 200 kV with a point resolution of 0.24 nm. Sample preparation included dilution of 2 drops of the IL phase in ~1.5 mL of MeCN, followed by deposition on a carbon-coated copper grid (400 mesh) at rt.

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