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New approaches to fluorinated ligands and their application in catalysis

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Abstract—Simple and generic approaches to fluorous soluble ligands have been developed and applied to the synthesis of various fluorinated arylphosphines including polymeric ones. The utility of some of these ligands has been demonstrated in catalysis in supercritical CO_2 ($scCO_2$) and fluorous solvents.

1. Introduction

One of the current frontiers in homogeneous catalysis concerns the use as reaction media of non-traditional solvents such as water, ionic liquids, $scCO_2$ and perfluorocarbons.[1,2] For catalysis in some of these solvents, modifications to ligands are necessary in order to make their metal complexes soluble. A well established strategy for catalysis by organometallic complexes in $scCO_2$ and fluorous solvents is to attach long perfluoroalkyl chains to conventional ligand scaffolds.[1,3] Arylphosphines are probably the most widely used ligands in homogeneous catalysis.[2] Consequently, several approaches to perfluoroalkylated arylphosphines have been reported. Hope and co-workers synthesised such phosphines by the Cu-mediated coupling of iodobromobenzenes with perfluoroalkyl iodides followed by lithiation with *n*-BuLi at −78°C and reaction with $PPh_{3-n}Cl_n$ (Scheme 1).[3h,p] Knochel prepared these arylphosphines via a similar route; but the perfluoroalkyl substituted bromobenzene was obtained by the Sandmeyer reaction.[3n] Fluorous arylphosphines, which contain an ethylene spacer between the aromatic ring and the perfluoroalkyl group, were first synthesised by Leitner and co-worker via the copper-catalysed coupling of a mono Grignard reagent derived from a dibromobenzene with 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl iodides followed by the familiar reactions.[3o] Improved methods for making related fluoroalkylated aromatic bromides have recently been reported by Gladysz[3a] and Curran.[3b] van Koten has developed a route to fluorous arylphosphines, where the fluorous moiety is introduced by the reaction of dibromobenzene with a fluorinated silane.[3c,k] While these methods have played an important role in developing fluorinated ligands and catalysis in $scCO_2$ and fluorous solvents, none is without disadvantages. In all the methods, for instance, the perfluoroalkyl reagents, often the most expensive of all reagents involved, are introduced in the first step of synthesis, thus resulting in relatively inefficient utilisation of these reagents. In addition, moisture-sensitive and pyrophoric reagents and low temperature are often employed, and some intermediates have proven difficult to purify.[4] To some degree, the difficulty in the synthesis of fluorous phosphines has impeded the exploration of catalysis in $scCO_2$ and fluorous solvents. Therefore, the design of efficient synthetic routes for the fluoroalkylation of ligands including in particular phosphines is of significant importance to the further development of catalytic processes in emerging solvents. Simple and high-yield methods to arylphosphines bearing perfluorinated ponytails have recently been developed in our lab, the details of which are herein described.[5] A brief description of their application in catalysis in fluorous phases and $scCO_2$ is also given.

2. Results and discussion

Metal catalysed and mediated C–C coupling reactions have been widely used in organic synthesis.[6] We have succeeded in applying the chemistry to the synthesis of phosphine and related ligands, soluble not only in $scCO_2$ and fluorous solvents but in water and ionic liquids as well. Our strategy is based on the coupling of haloarylphosphine oxides, e.g. $OPPh_{3-n}(C_6H_4Br)_n$ (n=1–3), with alkyl halides, olefins, organoboranes, amines and alcoholic substrates (Scheme 2). In the particular case of fluorous arylphosphines, C–C coupling of the haloarylphosphine oxides with fluorinated alkyl halides and olefins readily furnishes the desired ligands.

2.1. Synthesis of perfluoroalkylated arylphosphines by copper-mediated coupling

Copper-mediated cross coupling of perfluoroalkyl iodides

Keywords: fluorinated ligands; fluorinated phosphines; fluorinated polymers; C–C coupling; fluorous catalysis; supercritical CO_2.

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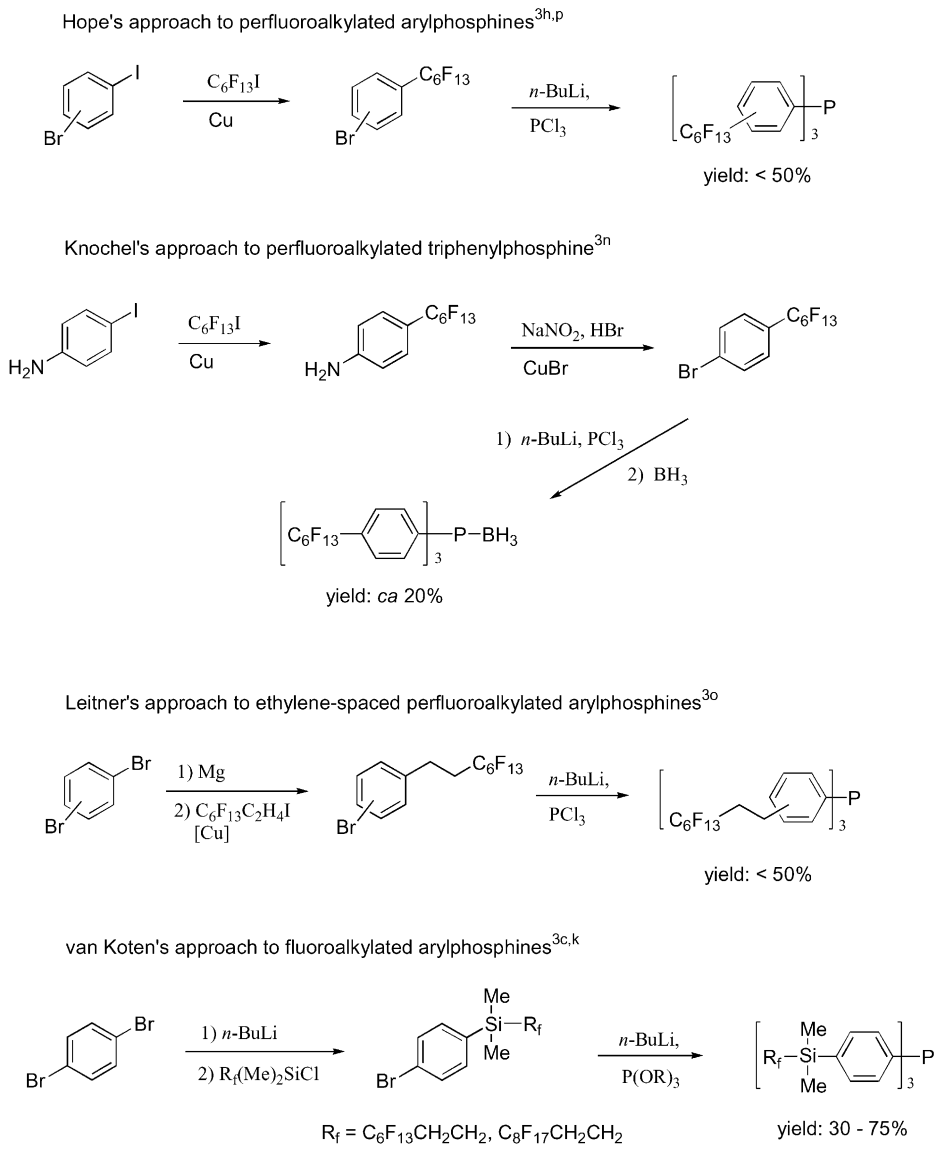
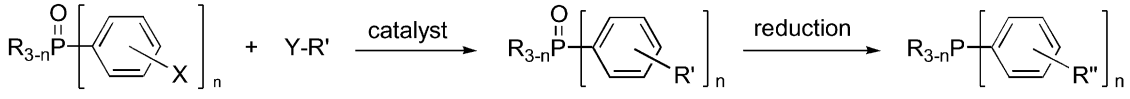
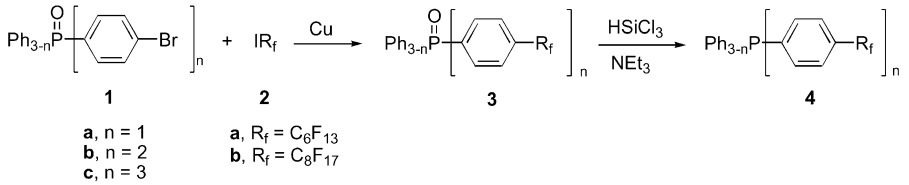


Scheme 1. Literature approaches to fluorinated arylphosphines.

with iodoaromatic compounds to give perfluoroalkyl-substituted aromatics was first reported by McLoughlin and Thrower.[7] The reaction was later extended to include bromoaromatics and shown to tolerate functional groups such as OH, CO_2R, and NH_2.[8] Prompted by these early findings, we attempted the coupling of the haloarylphosphine oxides **1** with perfluoroalkyl iodides **2** (Scheme 3). Since these phosphine oxides are easily available starting from 1,4-dibromobenzene and phosphorus chlorides and require no special precautions to handle,[9] such a reaction was anticipated to offer a much simplified route to perfluoroalkylated phosphines.[5a] The coupling of $OPPh_{n-3}$-(4-$C_6H_4Br)_n$ (n=1–3) **1** with IC_6F_{13} **2a** proceeded smoothly in the presence of copper powder to give the perfluorohexyl-substituted phosphine oxides $OPPh_{n-3}(4\text{-}C_6H_4C_6F_{13})_n$ **3** in greater than 90% isolated yields. Table 1 summarises the results. The obtained yields are remarkable, as most previously reported coupling reactions of aryl iodides and bromides have yields lower than 70%.[7,8] The key to the success of the current method is the use of oxidised phosphines. When bromoarylphosphines were employed instead of the oxides, complex mixtures were obtained under otherwise identical reaction conditions. The presence of a catalytic amount of 2,2′-bipyridine (bipy) in the reaction lowers the reaction temperature without affecting the conversion and yield. Bipy may play a role in facilitating metallation of copper by **2**.[7] The phosphine oxide **1** may play a similar role, thus promoting higher yields at milder conditions. As with the coupling reactions of other haloaromatics, DMSO is the solvent of choice.[7,8] In DMF, the



Scheme 2. Metal catalysed or mediated functionalisation of arylphosphies (n=1–3).

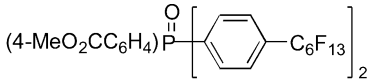


Scheme 3. Synthesis of perfluoroalkylated arylphosphines by Cu-mediated cross-coupling.

reaction was sluggish and less clean. The chloride analogues $OPPh_{n-3}(4\text{-}C_6H_4Cl)_n$ failed to react. Longer reaction time was required on going from **1a** to **1c** due to increasing substitution by the perfluorohexyl moiety and accompanied decrease in solubility of **3** in the solvent. Solubility appears also to be responsible for the slightly lower yield obtained with **3ca**. Thus, when the reaction was carried out in a perfluoro-1,3-dimethylcyclohexane and DMSO (10:1, v/v) mixture, the yield of **3ca** increased to 95%. Solubility was even more a problem with the longer IC_8F_{17} **2b**. Thus, when the reaction of **1c** with **2b** was performed in DMSO, a yield of only 45% was obtained for **3cb**. Remarkably, when performed in the perfluoro-1,3-dimethylcyclohexane and DMSO mixture, the reaction proceeded to give the substituted product in 93% isolated yield. Whilst the coupling reactions above were performed under nitrogen, they can also be carried out in air without notable effects on yields. More recently, we have found that a mixture of benzotrifluoride and DMSO (10:1, v/v) is even better for this coupling. Benzotrifluoride is not expensive, and it dissolves both the starting materials and products under the reaction condition. The work up is also made simpler. Thus, pure product can be easily obtained by filtering off the excess copper and copper salts followed by washing with 1N HCl and water to remove the remaining copper salts and DMSO and then drying (Table 1).

The phosphines were released from the oxides by reduction with trichlorosilane.[10] The reaction was carried out by simply heating a mixture of a perfluoroalkylated phosphine oxide **3**, trichlorosilane, and triethylamine in toluene at 120°C for a few hours, affording the free phosphines **4aa**, **ba**, **ca**, and **cb** in almost quantitative isolated yields (Table 1). Hence, about 90% of the perfluoroalkyl reagents can effectively be incorporated into the desired product. In contrast, previous methodologies led to less efficient use of the expensive perfluoroalkyl iodides.[3h,n–p]

The compatibility of the method with functional groups can, to some degree, be judged by the coupling of **2a** with methyl 4-[di(4-bromophenyl)phosphinyl]benzoate **5**, yielding methyl 4-[di(4-perfluorohexylphenyl)phosphinyl]benzoate **6** in 92% isolated yield. The free phosphine derived from **6** would be amphiphilic and immobilizable.



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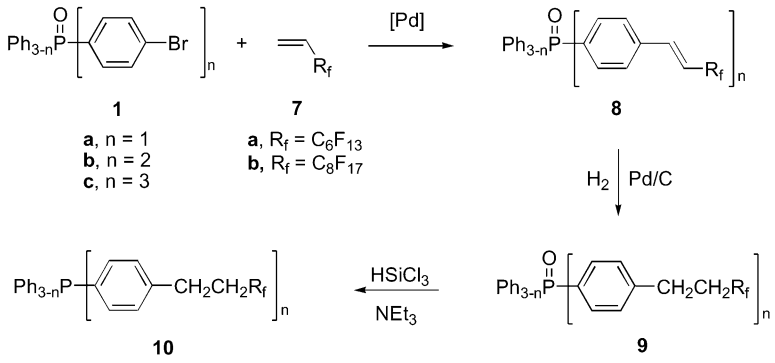
2.2. Synthesis of fluoroalkylated arylphosphines by the Heck reaction

The direct coupling of perfluoroalkyl iodides with haloarylphosphine oxides mediated by copper is an efficient approach to arylphosphines bearing perfluorinated ponytails. However, this method does not allow one to introduce an ethylene spacer between the aromatic ring and the perfluoroalkyl unit, which is often necessary to reduce the strong electron-withdrawing effect of the latter. As indicated above, the previous methods to these ligands have met with difficult separation problems. Since the Heck reaction provides probably the most convenient way for the olefination of aromatic halides, we thought that the coupling of haloarylphosphine oxides with fluorinated olefins could lead to the easy preparation of various fluorous arylphosphines containing ethylene spacers.[5b] In fact, the preparation of β-trifluoromethylstyrene via the Heck reaction of aryl halides with trifluoropropene was reported two decades ago.[11]

Table 1. Synthesis of perfluoroalkylated arylphosphines via copper-mediated coupling of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ with IR_f followed by reduction with $HSiCl_3$

Compound	Solvent	*n*	R_f	Temperature (°C)	Time (h)	Yield (%)[a]
3aa	DMSO	1	C_6F_{13}	120	15	95
3ba	DMSO	2	C_6F_{13}	120	24	94
3ca	DMSO	3	C_6F_{13}	120	36	91
3cb	DMSO	3	C_8F_{17}	120	36	45
3cb	PFCy[b]	3	C_8F_{17}	110	72	93
3ca	BTF[c]	3	C_6F_{13}	115	24	92
3cb	BTF[c]	3	C_8F_{17}	115	24	93
4aa	Toluene	1	C_6F_{13}	120	6	97
4ba	Toluene	2	C_6F_{13}	120	6	98
4ca	Toluene	3	C_6F_{13}	120	6	98
4cb	Toluene	3	C_8F_{17}	120	6	95

For detailed reaction conditions, see Section 3.
[a] Isolated yield.
[b] Perfluoro-1,3-dimethylcyclohexane (PFCy)+DMSO (10:1, v/v).
[c] Benzotrifluoride (BTF)+DMSO (10:1, v/v).



Scheme 4. Synthesis of fluoroalkylated arylphosphines by the Heck reaction.

To our delight, the oxides **1** could easily be olefinated with the fluorinated olefins **7** to give the olefinated phosphine oxides **8** (Scheme 4). In a typical reaction, a phosphine oxide **1** was mixed with 1.1 equiv. of an olefin **7** (relative to bromine), ca. 1.3 equiv. of NaOAc, and 0.5–1 mol% of the Herrmann–Beller palladacycle catalyst in DMF.[12] The coupling reaction proceeded smoothly at 125°C to give **8** in more than 90% isolated yields without optimisation (Table 2). In all the cases, the reaction completed in 24 h reaction time regardless of the number of bromo groups in the starting oxide. The O═P substituted phenylbromides thus behave like an activated arylbromide such as 4-bromoacetophenone in the Heck reaction. Activation of bromobenzene itself requires more stringent conditions with the same palladacycle catalyst. This may not be surprising given the strong electron withdrawing capability of the O═P moiety.[13] ^{1}H NMR studies indicate that the electron withdrawing effect of the phosphoryl group on the *para* position of a phenyl ring lies between those of a carbonyl and a bromide group.[9] In line with this argument, tris-(4-bromophenyl)phosphine failed to couple with **7a** under conditions similar to those employed for the corresponding oxide, although this could also arise from possible poisoning of active palladium species by the excessive phosphine, and the borane protected tris(4-bromophenyl)phosphine did not react either with the same olefin. As with other Heck reactions, substitution of the vinylinic protons by the arylphosphine oxides occurs at the less substituted side of the C═C double bond leading to *trans* olefins.

To obtain the free phosphines **10**, the substituted phosphine oxides **8** were first subjected to hydrogenation and then reduced by treatment with trichlorosilane as described above for **4**. As an example, the hydrogenation of **8ca** catalysed by Pd/C under 10 bar H_2 afforded the saturated oxide **9ca**. ^{1}H and ^{31}P NMR spectra of the oxide so obtained showed no by-products. The oxide can therefore be taken directly to the next step for reduction after filtering off the Pd/C catalyst and removal of solvent. The reduction of **9ca** by trichlorosilane afforded the free phosphine **10ca** in 96% isolated yield. Other free phosphines were obtained in similar yields. Thus, the ethylene spaced, perfluoroalkylated arylphosphines could easily be accessed via the Heck reaction, and close to 90% of the perfluoroalkyl reagents has been incorporated into the desired product with the present methodology.

Table 2. Heck olefination of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ with $H_2C{=}CHR_f$

Compound	*n*	R_f	Time (h)	Yield (%)[a]
8aa	1	C_6F_{13}	20	93
8ba	2	C_6F_{13}	24	94
8ca	3	C_6F_{13}	24	91
8cb	3	C_8F_{17}	24	92

For detailed reaction conditions, see Section 3.
[a] Isolated yield.

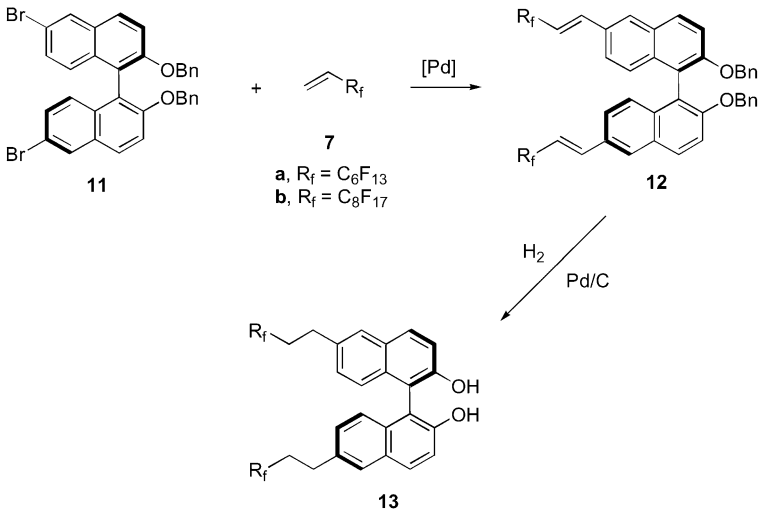
2.3. Synthesis of perfluoroalkylated BINOLs by the Heck reaction

The Heck reaction above could also be extended to the fluorination of optically active binaphthols (BINOLs), which have extensively been used as ligands or building blocks for ligands in asymmetric catalysis (Scheme 5).[6] Thus in the presence of 0.5 mol% of the palladacycle catalyst, the Heck reaction of (*R*)-6,6′-dibromo-2,2′-dibenzyloxy-1,1′-binaphthyl **11** with **7a** was complete in 24 h reaction time at 125°C to give the expected *trans* substituted product **12a** in 95% isolated yield. Following hydrogenation by Pd/C to reduce the double bonds and debenzylate at the same time, the fluoroalkylated (*R*)-1,1′-bi-2-naphthol **13a** was obtained in 86% overall yield. The coupling involving **7b** with a longer fluorous chain worked equally well, affording the substituted binaphthol **13b** in 82% overall yield. Whilst the Heck reaction by the palladacycle catalyst generally requires high temperature and long reaction time with deactivated arylbromides such as alkoxy substituted bromobenzenes,[12] the reactivity of the binaphthol derivative **11** appears to be similar to activated aryl bromides.

The fluoroalkylated (*R*)-1,1′-bi-2-naphthol **13** can be used for the synthesis of fluoroalkylated BINAP.[14] Other perfluoroalkylated aromatic building blocks have also been prepared by us by this methodology.[15] In a related development, multi-fluoroalkylated BINOLs were synthesised via the organolithium mediated reaction of a 6,6′-dibromo-1,1′-bi-2-naphthol derivative with a fluoroalkylated bromosilane[16] and the copper mediated coupling of a 4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol derivative with a perfluoroalkyl iodide.[17]

2.4. Synthesis of fluorous soluble polymeric arylphosphines

The application of fluorous ligands in catalysis in fluorous solvents and $scCO_2$ is often complicated by the finite

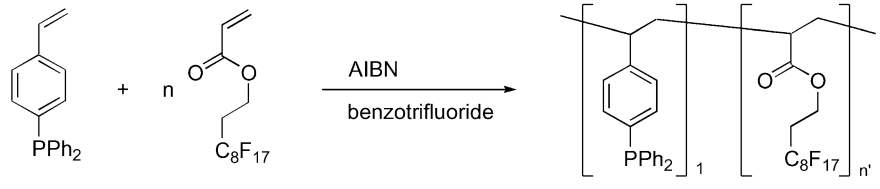


Scheme 5. Synthesis of chiral fluoroalkylated BINOLs by the Heck reaction.

solubility of such ligands in common organic solvents, which makes catalyst recycle more difficult than one would expect if the ligands could completely be immobilised in one phase. This is particularly true for fluoroalkylated arylphosphines such as $P(4\text{-}C_6H_4CH_2CH_2C_6F_{13})_3$ **10ca**. These are more soluble in organic solvents than are analogous perfluoroalkylphosphines such as $P(CH_2CH_2C_6F_{13})_3$ and thus less useful in fluorous biphasic catalysis.[1f] Ironically, it is the former class of phosphines that are far more extensively used in homogeneous catalysis. In order to further improve the solubility of arylphosphines in fluorous solvents and $scCO_2$ and reduce their solubility in normal organic solvents so that easier catalyst/product separation could be attained, we designed and synthesised fluorous polymer-supported arylphosphines as an alternative to fluorous soluble molecular ligands such as **4** and **10**.[18] A fluoroacrylate copolymer containing alkylarylphosphine groups has recently been reported and shown to be effective in rhodium catalysed hydrogenation of olefins, while this work was in progress.[3e]

The poly[fluoroacrylate-*co*-4-(diphenylphosphino)styrene] ligands **16** and **17** were synthesised by radical copolymerisation of 4-(diphenylphosphino)styrene **14** with 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate **15** at 65°C in the presence of AIBN in benzotrifluoride (Scheme 6). For the fluorous polymer **16**, the molar ratio of **15** to **14** was 5:1. For **17**, the ratio was 9:1. After removal of benzotrifluoride, the resultant solid was washed with hot toluene, affording the polymers as white powders in greater than 90% yields. The IR spectrum of both polymers showed disappearance of absorptions due to C=C stretching, in line with the lack of resonance due to olefinic protons in the ^1H NMR spectrum. The C=O absorption appeared at 1738 cm^{-1} for **16** and 1740 cm^{-1} for **17** in the IR spectrum. The ^{31}P NMR spectrum of each polymer in benzotrifluoride (containing 5% $CDCl_3$) displayed a relatively sharp singlet at around δ −6.2. Surprisingly, the singlet became much broader in perfluoro-1,3-dimethylcyclohexane, with half-height line width of 200 Hz as opposed to 58 Hz in benzotrifluoride for **16**. The polymers are soluble in both solvents. One possible explanation for the line broadening is that in perfluorinated solvents the polymers, which contain both fluorous-soluble and insoluble segments, may aggregate, whereas in partly fluorinated solvents such as benzotrifluoride such aggregation may not be favoured due to favourable solvent–solute interactions.[19] The phosphorus content of the polymers was estimated to be 1.2% for **16** and 0.8% for **17** by ^{31}P NMR using bis(diphenylphosphino)methane as an internal standard. These values are close to the value of 1.1 and 0.6% calculated on the basis of the monomer ratios, and are consistent with the high yields of polymer synthesis.

As is expected, the fluorous soluble polymer-supported arylphosphine ligands are much less soluble in common organic solvents than are molecular arylphosphines modified with fluorous ponytails. This is evident from the approximate partition coefficient *f* shown in Table 3. The partition coefficient is defined as the ratio of the weight of a polymer in fluorous phase vs that of the same polymer in an organic solvent under equilibrium conditions. The partition coefficient for **16** is ca. 27 and does not vary significantly with the organic solvents. In contrast, the values of *f* for the



Scheme 6. Synthesis of fluorous soluble polymer-supported arylphosphines.

Table 3. Partition coefficients of phosphines in organo-fluorous phases

Phosphine	Solvent[a]	f[b]
16	Toluene/PFCy	26.9
	THF/PFCy	27.7
P(4-$C_6H_4C_6F_{13})_3$ **4ca**	Toluene/PFCy	4.4
	THF/PFCy	2.2
P(4-$C_6H_4CH_2CH_2C_6F_{13})_3$ **10ca**	Toluene/PFCy	0.9
	THF/PFCy	0.2

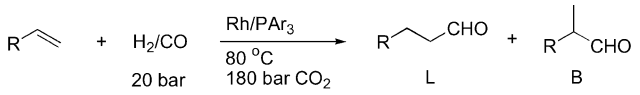
Measured at 24°C by first saturating an organo/perfluorocarbon solvent mixture with the ligand under question followed by syringing equal volume solution from the two phases and by weighing the dried and solvent-free ligand.
[a] PFCy=perfluoro-1,3-dimethylcyclohexane.
[b] f=weight of ligand in fluorous phase/weight of ligand in organo phase.

molecular ligand P(4-$C_6H_4C_6F_{13})_3$ **4ca** are much smaller, and are still smaller for the ethylene-spaced P(4-$C_6H_4CH_2CH_2C_6F_{13})_3$ **10ca**. The latter is in fact more soluble in the organic solvents than in the perfluorinated solvents. Clearly, for fluorous biphasic catalysis involving fluorous soluble arylphosphine ligands, **16** and **17** would offer a better choice for retaining a metal catalyst in the fluorous phases.

2.5. Hydroformylation of olefins in $scCO_2$

Hydroformylation is one of the most important applications of homogeneous catalysis in industry. A number of publications concerning this reaction have appeared, striving for more active and selective rhodium catalysts coupled with easy catalyst separation and reuse.[2] In this context, $scCO_2$ has proven to be an excellent medium, offering high reaction rates and the potential of easy catalyst/product separation.[20] Our work in this area has recently been published.[21] We summarise below only the salient aspects of the observations.

As is well known and evident from the above, fluoroalkylation of common phosphines provides an easy entry into ligands soluble in $scCO_2$ and perfluorocarbons.[1,3] Indeed, phosphines bearing fluorinated ponytails such as $P(CH_2CH_2C_6F_{13})_3$ and **10ca** have been shown, when combined with rhodium, to be effective and recyclable in hydroformylation in these non-conventional solvents.[20d,22] Due to the strong electron-withdrawing effect of the perfluoroalkyl substituents, a spacer group such as methylene units is normally employed to insulate the phosphorus



PAr_3	TOF, h^{-1}	L/B
4ca	2963	3.6
10ca	957	3.6
18	150	4.5

Scheme 7. Effect of phosphine ligands on rhodium-catalysed hydroformylation of 1-hexadecene in $scCO_2$. Reaction conditions: 1.5–3.0 μmol [Rh(acac)$(CO)_2$], 10 equiv. of PAr_3, olefin concentration 0.15 M, reaction time 1 h. **18**=P(4-$C_6H_4C_6H_{13})_3$. For more details, see Ref. 21c.

R	Solvent	TOF, h^{-1}
Me	$scCO_2$	1593
Bu	$scCO_2$	1671
t-Bu	$scCO_2$	1827
Me	toluene	92
Bu	toluene	84
t-Bu	toluene	191

Scheme 8. Rhodium/**4ca**-catalysed hydroformylation of alkyl acrylates in $scCO_2$ (180 bar CO_2) and toluene. Reaction conditions: 3.9–6.3 μmol [Rh(acac)$(CO)_2$], 10 equiv. of **4ca**, methyl acrylate concentration 0.45 M, butyl and *t*-butyl acrylate concentration 0.28 M, reaction time 1 h. For more details, see Ref. 21b.

from the perfluoroalkylated ponytails.[1,3] However, our investigation shows this not to be necessary for hydroformylation in $scCO_2$.[21c]

Our results on the hydroformylation of 1-hexadecene obtained with arylphosphines containing three differing ponytails are depicted in Scheme 7. The hydroformylation reactions in $scCO_2$ were performed for 1 h using a combination of [Rh(acac)$(CO)_2$] and 10 equiv. of a phosphine ligand at 80°C, 20 bar H_2/CO (1:1), and 180 bar CO_2. As is evident, the ponytails impose a significant effect on the activity of rhodium, as can be judged by the average turnover frequency (TOF) to aldehyde. Thus, on going from the perfluoroalkylated ligand **4ca** to the ethylene-spaced **10ca**, the rates of the hydroformylation decreased ca. 3 times. The same trend also holds for other 1-alkenes. Hence, it is clear that insulating spacer groups are not necessary and in fact bring about detrimental effect on rates in hydroformylation in $scCO_2$. Because both ligands are soluble and form a homogeneous solution in $scCO_2$ under the reaction conditions and because they are sterically similar, the observed decrease in rates can only be attributed to an increase in the electron richness of the phosphorus in **10ca**. In line with this explanation, the fully alkylated ligand P(4-$C_6H_4C_6H_{13})_3$ **18** yielded a still lower TOF, although the low solubility of **18** in $scCO_2$ undoubtedly also contributed to the decreased TOF. These observations are not surprising. Previous investigations in conventional solvents have shown that triarylphosphines and related bidentate ligands bearing electron-withdrawing substituents tend to give higher rates and better regioselectivities to linear aldehydes.[23] The regioselectivity of the reactions in Scheme 7, as measured by the linear/branched (L/B) aldehyde ratios, did not increase with increasing electron-withdrawing power of the ponytails, however.

Our second example concerns the hydroformylation of acrylic esters in $scCO_2$. This is potentially a synthetically useful reaction, as it produces bifunctional compounds that can be used as intermediates for synthesis. However, in common organic solvents the reaction is in general slow and high temperature and/or high pressure are often required.[24] In sharp contrast, the reaction is found to be

fast and regioselective as well when run in $scCO_2$ in the presence of [Rh(acac)$(CO)_2$] and **4ca** (Scheme 8).[21b]

As can be seen, the average TOFs for the formation of aldehydes in the hydroformylation of the three acrylates in $scCO_2$ ranged from 1593 to 1827 h^{-1}. For comparison, in toluene under otherwise identical reactions conditions, the TOFs were less than 200 h^{-1}. The linear aldehyde product could hardly be detected by GC in these reactions. Thus, by simply changing the reaction medium from toluene to $scCO_2$, the TOF values increased ca. 10–20 fold. Such dramatic enhancement in reaction rates by $scCO_2$ has rarely been observed before, although the high miscibility of various gases with CO_2 and its excellent transport properties have often been suggested to be impetus for fast reactions.[1a] A further demonstration of the rate enhancement is the hydroformylation of an equimolar mixture of butyl acrylate and 1-decene by the same catalyst in $scCO_2$. The TOFs observed for butyl acrylate and 1-decene were 1511 and 379 h^{-1}, respectively. This is remarkable, considering that in the absence of the acrylate the average TOF for 1-decene was 2794 h^{-1} under otherwise identical reaction conditions.[21c] In a similar experiment in toluene, the TOF was found to be 56 for the acrylate and 24 h^{-1} for 1-decene, while in the absence of the acrylate the TOF for the latter olefin rose to 901. Evidently, the Rh-**4ca** catalyst is considerably more chemoselective towards the less reactive acrylates, but it is only in $scCO_2$ in which it becomes highly active as well!

The promoting effect of CO_2 may stem from its possible specific interactions with the solute. The rate-determining step in the acrylate hydroformylation has been proposed to be the opening of a thermodynamically stable five-membered chelate ring formed by the coordination of the acrylate carbonyl oxygen to rhodium.[25] In $scCO_2$, this opening could be made easy by carbonyl–CO_2 donor–acceptor and Rh–CO_2 covalent interactions. Previous spectroscopic studies have already shown that carbonyl groups can act as Lewis bases and interact with CO_2 acting as a Lewis acid.[26] Such specific solvent–solute interactions have rarely been exploited in catalysis in $scCO_2$ but could provide a unique means for tuning chemical activity and selectivity in synthesis in $scCO_2$.

2.6. Fluorous biphasic hydroformylation with fluorous soluble polymer ligands

The applicability of the fluorous soluble polymer ligands **16** and **17** was also tested in the hydroformylation of olefins such as 1-alkenes, styrene and acrylates, but under fluorous biphasic conditions (solvent: hexane–toluene–perfluoromethylcyclohexane, 2:1:2, v/v) instead of using $scCO_2$. The results have been described before.[18] The salient features of the results are: firstly, the activity of the fluorous soluble polymer catalyst Rh-**16** and Rh-**17** are significantly higher than that reported for solid polymer- and aqueous soluble polymer-supported rhodium catalysts.[27] Secondly, as with solid polymer-supported catalysts, the aldehyde L/B ratio is markedly higher than achievable with similar P/Rh ratios when using homogeneous rhodium–phosphine catalysts. Thirdly, smaller olefins appear to give higher turnovers, probably owning to better miscibility between the olefins and the fluorous phase. Thus, while the hydroformylation of 1-hexadecne by Rh-**16** gave a TON (turnover number, mole of aldehyde formed per mol of rhodium) of 1640 at 100°C and 30 bar H_2/CO in a 12 h reaction time, the reaction with 1-hexene yielded a TON near 140,000 by the same catalyst at 100°C and 50 bar H_2/CO in 58 h.

As indicated earlier, one of the objectives for synthesising **16** and **17** was to lower the miscibility of their metal complexes with organic solvents such that the catalyst/product separation and catalyst reuse could be facilitated. The recyclability of the rhodium catalyst containing the fluoropolymer **16** was examined in the hydroformylation of 1-hexene. At 100°C and 50 bar H_2/CO with olefin/Rh=48,000, three consecutive hydroformylation reactions were run, giving an excellent combined TON of 70,000 and an average aldehyde selectivity of 99%. A 1 ppm loss of rhodium accompanied with a 6% decrease in conversion in the recycle experiment was measured. This loss in rhodium and in catalyst activity appears to be largely due to the finite miscibility of the substrate/product with the fluorous solvent. At the end of the third run, all the perfluoromethylcyclohexane had leached to the product phase, thus making the polymer catalyst partially soluble in the product. By optimising the operating conditions, e.g. by varying the organic solvent, the problem of rhodium leach could be minimised.

In summary, we have devised a generic approach for the synthesis of arylphosphines that can be applied as soluble ligands for catalysis in $scCO_2$ and fluorous solvents. The synthesis centres on catalytic C–C coupling chemistry, and is simpler and more economical than the currently available methods. The feasibility of the approach is manifested by the various ligands that have been prepared in our lab. The easy availability of these ligands makes more feasible to evaluate metal/ligand combinations for catalytic reactions in such ecologically attractive solvents as $scCO_2$. Our demonstration of the remarkable difference between **4ca** and the ethylene-spaced **10ca** in hydroformytaion in $scCO_2$ serves as a good example.

3. Experimental

3.1. General remarks

All reactions were performed under an inert atmosphere. Melting points were determined in a capillary tube on a Gallenkamp apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 or a Bruker Avance 400 spectrometer in $CDCl_3$ with TMS as internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM 250 spectrometer in $CDCl_3$ with 85% H_3PO_4 as external standard. Optical rotations were measured with a Polaar 2001 polarimeter, and MS spectra on a VG7070E mass spectrometer. Elemental analysis was performed by Butterworth Laboratories Ltd. Flash chromatography was performed using ICN Silica 32-63. Toluene and benzotrifluoride were distilled over CaH_2 and P_2O_5 under nitrogen, respectively. 1-Iodoperfluorohexane **2a**, 1-iodoperfluorooctane **2b**, 1*H*,1*H*,2*H*-perfluoro-1-octene **7a**, 1*H*,1*H*,2*H*-perfluoro-1-decene **7b**, and 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate

15 were purchased from Apollo Scientific Ltd and used without further purification. The bromophenylphosphine oxides $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ (n=1–3) **1a–c**[9] and the Herrmann–Beller Palladacycle were prepared according to published procedures.[12]

3.2. Synthesis of fluoroalkylated arylphosphine oxides and the free phosphines

3.2.1. Tris(4-perfluorohexylphenyl)phosphine oxide (3ca). A mixture of **1c** (515 mg, 1.0 mmol), **2a** (1.405 g, 3.2 mmol), copper powder (450 mg, 7.1 mmol), 2,2′-bipyridine (34 mg, 0.2 mmol), DMSO (1.0 ml, 14.1 mmol), and benzotrifluoride (10 ml) was stirred and refluxed for 24 h. The mixture was then cooled to room temperature, filtered through a pad of Celite and washed with $CHCl_3$ (2×20 ml). The combined filtrates were washed successively with 1N HCl (2×50 ml), water (50 ml) and brine (30 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The resultant solid was crystallised from EtOH to give **3ca** as colourless needles (1.133 g, 92%). Mp 136–138°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (dd, 6H, J=8.3 and 2.1 Hz), 7.84 (dd, 6H, J=11.4 and 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 127.5 (dt, $^3J_{C-P}$=11.6 Hz and $^3J_{C-F}$=6.6 Hz), 132.3 (d, $^2J_{C-P}$=10.2 Hz), 133.4 (dt, $^2J_{C-F}$=21.1 Hz and $^4J_{C-P}$=2.4 Hz), 135.6 (d, $^1J_{C-P}$=101.7 Hz);[28] ^{31}P NMR ($CDCl_3$, 101 MHz): δ 25.6 (s); Anal. calcd for $C_{36}H_{12}F_{39}PO$: C, 35.09; H, 0.98. Found: C, 35.35; H, 0.97. In the ^{13}C NMR spectrum of **3ca** and those of others, signals due to carbons of the fluorocarbon chains were too weak to be assigned.

3.2.2. (4-Perfluorohexylphenyl)diphenylphosphine oxide (3aa). 3aa was prepared from **1a** and **2a** in the same way as for **3ca** in 95% isolated yield. Mp 121–123°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.78 (m, 12H), 7.83 (dd, 2H, J=11.3 and 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 127.3 (dt, $^3J_{C-P}$=12.1 Hz and $^3J_{C-F}$=6.4 Hz), 128.9 (d, $^3J_{C-P}$=11.6 Hz), 129.1 (d, $^3J_{C-P}$=12.7 Hz), 132.0 (d, $^1J_{C-P}$=104.0 Hz), 132.4 (d, $^2J_{C-P}$=9.5 Hz), 132.7 (td, $^2J_{C-F}$=21.3 Hz and $^4J_{C-P}$=2.4 Hz), 137.9 (d, $^1J_{C-P}$=101.1 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 28.4 (s); Anal. calcd for $C_{24}H_{14}F_{13}PO$: C, 48.34; H, 2.37. Found: C, 48.69; H, 2.40.

3.2.3. Bis(4-perfluorohexylphenyl)phenylphosphine oxide (3ba). 3ba was prepared from **1b** and **2a** in the same way as for **3ca** in 94% isolated yield. Mp 114–116°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51–7.70 (m, 5H), 7.73 (dd, 4H, J=8.2 and 2.0 Hz), 7.84 (dd, 4H, J=11.4 and 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 127.3 (dt, $^3J_{C-P}$=12.1 Hz and $^3J_{C-F}$=6.4 Hz), 129.0 (d, $^3J_{C-P}$=12.4 Hz), 130.7 (d, $^1J_{C-P}$=105.5 Hz), 132.0 (d, $^3J_{C-P}$=11.0 Hz), 132.4 (d, $^2J_{C-P}$=10.2 Hz), 132.9 (td, $^2J_{C-F}$=21.3 Hz and $^4J_{C-P}$=2.4 Hz), 136.6 (d, $^1J_{C-P}$=101.1 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 26.8 (s); Anal. calcd for $C_{30}H_{13}F_{26}PO$: C, 39.41; H, 1.43. Found: C, 38.92; H, 1.30.

3.2.4. Tris(4-perfluorooctylphenyl)phosphine oxide (3cb). 3cb was prepared from **1c** and **2b** in the same way as for **3ca** in 93% isolated yield. Mp 138–140°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (dd, 6H, J=8.3 and 2.1 Hz), 7.84 (dd, 6H, J=11.4 and 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.3 (dt, $^3J_{C-P}$=12.1 Hz and $^3J_{C-F}$=6.4 Hz), 133.4 (d, $^2J_{C-P}$=10.4 Hz), 135.0 (td, $^2J_{C-F}$=21.3 Hz and $^4J_{C-P}$=2.4 Hz), 136.0 (d, $^1J_{C-P}$=101.7 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 25.7 (s); Anal. calcd for $C_{42}H_{12}F_{51}PO$: C, 32.92; H, 0.79. Found: C, 32.84; H, 0.83; MS (CI, m/z): 1533 (M^++1), 1115, 1074, 1054, 1036, 1023.

3.2.5. Tris(4-perfluorohexylphenyl)phosphine (4ca). A mixture of **3ca** (2.465 g, 2.0 mmol), trichlorosilane (4.064 g, 30 mmol), triethylamine (4.554 g, 15 mmol), and toluene (20 ml) was stirred at 120°C for 6 h under nitrogen. The mixture was cooled to room temperature and further cooled with an ice bath. Saturated $NaHCO_3$ aqueous solution (1 ml) was added and the mixture stirred for 10 min. The solution was then filtered through a short alumina column, and washed with hexane. The filtrate was evaporated under reduced pressure to afford **4ca** as a white solid (2.384 g, 98%). Mp 66–68°C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.42 (dd, 6H, J=8.2 and 7.7 Hz), 7.61 (d, 6H, J=7.7 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ −6.1 (s). **4ca** has previously been reported.[3p]

3.2.6. (4-Perfluorohexylphenyl)diphenylphosphine (4aa). 4aa was prepared from **3aa** in the same way as for **4ca** in 97% isolated yield. Mp 75–78°C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.26–7.62 (m, 14H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ −5.3 (s). This compound has also been described in Ref. 3p.

3.2.7. Bis(4-perfluorohexylphenyl)phenylphosphine (4ba). 4ba was prepared from **3ba** in the same way as for **4ca** as a colourless oil in 98% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.24–7.65 (m, 13H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ −5.5 (s). This compound has also been described in Ref. 3p.

3.2.8. Tris(4-perfluorooctylphenyl)phosphine (4cb). 4cb was prepared from **3cb** in the same way as for **4ca** in 95% isolated yield. Mp 83–86°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (pseudo t or dd, 6H, J=8.0 Hz), 7.62 (d, 6H, J=8.0 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ −5.5 (s); Anal. calcd for $C_{42}H_{12}F_{51}P$: C, 33.27; H, 0.80. Found: C, 33.28; H, 0.63; MS (CI, m/z): 1517 (M^++1), 1037, 1022.

3.2.9. Methyl 4-[di(4-perfluorohexylphenyl)phosphinyl]-benzoate (6). 6 was prepared from methyl 4-[di(4-bromophenyl)phosphinyl]benzoate **5** and **2a** in the same way as for **3ca** in 92% isolated yield. Mp 156–158°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.96 (s, 3H), 7.75 (dd, 4H, J=8.4 and 3.0 Hz), 7.81 (dd, 4H, J=8.4 and 6.9 Hz), 7.86 (d, 2H, J=8.1 Hz), 8.18 (dd, 2H, J=8.1 and 3.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 52.6, 127.4 (dt, $^3J_{C-P}$=11.4 Hz and $^3J_{C-F}$=6.0 Hz), 129.9 (d, $^3J_{C-P}$=12.0 Hz), 132.1 (d, $^2J_{C-P}$=10.4 Hz), 132.3 (d, $^2J_{C-P}$=10.4 Hz), 133.2 (t, $^2J_{C-F}$=25.4 Hz), 134.2, 135.6 (d, $^1J_{C-P}$=102.7 Hz), 135.9 (d, $^1J_{C-P}$=101.6 Hz), 166.0; ^{31}P NMR ($CDCl_3$, 101 MHz): δ 26.2 (s); MS (FAB, m/z): 973 (M^++1), 781, 733, 674, 577; Anal. calcd for $C_{32}H_{15}F_{26}O_3P$: C, 39.53; H, 1.55. Found: C, 39.10; H, 1.38.

3.2.10. Tris[4-(1*H*,2*H*-perfluoro-1-octenyl)phenyl]phosphine oxide (8ca). A mixture of **1c** (1.03 g, 2.0 mmol), **7a** (2.284 g, 6.6 mmol), palladacycle (56 mg, 0.06 mmol), NaOAc (656 mg, 8.0 mmol), and DMF (10 ml) was stirred

for 24 h at 125°C. Most of DMF was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (100 ml) and water (100 ml). The organic layer was separated, washed with water (100 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, EtOAc–$CHCl_3$, 1:8) to give **8ca** as a pale-yellow oil (2.385 g, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.31 (dt, 3H, J=16.2 and 12.0 Hz), 7.22 (d, 3H, J=16.2 Hz), 7.60 (dd, 6H, J=8.2 and 2.5 Hz), 7.73 (dd, 6H, J=11.6 and 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 117.6 (t, $^2J_{C-F}$=23.5 Hz), 127.4 (d, $^3J_{C-P}$=12.5 Hz), 132.8 (d, $^2J_{C-P}$=10.4 Hz), 133.9 (d, $^1J_{C-P}$=103.7 Hz), 137.5, 138.5 (t, $^3J_{C-F}$=9.2 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 26.8 (s); Anal. calcd for $C_{42}H_{18}F_{39}PO$: C, 38.49; H, 1.38. Found: C, 38.24; H, 1.00; MS (CI, *m/z*): 1311 (M^++1), 1041, 967, 926, 890, 873.

3.2.11. [4-(1*H*,2*H*-Perfluoro-1-octenyl)phenyl]diphenylphosphine oxide (8aa). 8aa was prepared from **1a** and **7a** in the same way as for **8ca** in 93% isolated yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.30 (dt, 1H, J=16.2 and 12.0 Hz), 7.21 (d, 1H, J=16.2 Hz), 7.26–7.71 (m, 12H), 7.73 (dd, 2H, J=11.4 and 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 117.0 (t, $^2J_{C-F}$=23.2 Hz), 127.7 (d, $^3J_{C-P}$=12.5 Hz), 128.7 (d, $^3J_{C-P}$=12.1 Hz), 131.6, 132.1 (d, $^2J_{C-P}$=9.8 Hz), 132.3 (d, $^1J_{C-P}$=103.7 Hz), 132.8 (d, $^2J_{C-P}$=10.4 Hz), 135.6 (d, $^1J_{C-P}$=103.1 Hz), 136.8, 138.8 (t, $^3J_{C-F}$=9.4 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 27.7 (s); Anal. calcd for $C_{26}H_{16}F_{13}PO$: C, 50.18; H, 2.59. Found: C, 49.92; H, 2.43.

3.2.12. Bis[4-(1*H*,2*H*-perfluoro-1-octenyl)phenyl]phenylphosphine oxide (8ba). 8ba was prepared from **1b** and **7a** in the same way as for **8ca** in 94% isolated yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.31 (dt, 2H, J=16.1 and 12.0 Hz), 7.23 (d, 2H, J=16.1 Hz), 7.43–7.52 (m, 3H), 7.58 (dd, 4H, J=8.2 and 2.3 Hz), 7.65–7.68 (m, 2H), 7.73 (dd, 4H, J=11.6 and 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 117.5 (t, $^2J_{C-F}$=23.1 Hz), 128.0 (d, $^3J_{C-P}$=12.2 Hz), 129.1 (d, $^3J_{C-P}$=12.2 Hz), 132.1 (d, $^1J_{C-P}$=103.3 Hz), 132.6 (d, $^2J_{C-P}$=9.6 Hz), 132.7, 133.0 (d, $^2J_{C-P}$=10.1 Hz), 133.5 (d, $^1J_{C-P}$=103.1 Hz), 137.4, 138.9 (t, $^3J_{C-F}$=9.4 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 28.5 (s); Anal. calcd for $C_{34}H_{17}F_{26}PO$: C, 42.26; H, 1.77. Found: C, 42.38; H, 1.64; MS (CI, *m/z*): 967 (M^++1), 546.

3.2.13. Tris[4-(1*H*,2*H*-perfluoro-1-decenyl)phenyl]phosphine oxide (8cb). 8cb was prepared from **1c** and **7b** in the same way as for **8ca** in 92% isolated yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.32 (dt, 3H, J=16.2 and 12.0 Hz), 7.23 (d, 3H, J=16.2 Hz), 7.60 (dd, 6H, J=8.2 and 2.5 Hz), 7.73 (dd, 6H, J=11.6 and 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 117.6 (t, $^2J_{C-F}$=23.5 Hz), 128.0 (d, $^3J_{C-P}$=12.7 Hz), 133.0 (d, $^2J_{C-P}$=10.4 Hz), 134.1 (d, $^1J_{C-P}$=103.7 Hz), 137.6, 138.8 (t, $^3J_{C-F}$=9.2 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 26.9 (s). MS (FAB, *m/z*): 1611 (M^++1), 1167, 799, 723.

3.2.14. Tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phenyl]phosphine oxide (9ca). A mixture of **8ca** (2.611 g, 2.0 mmol), 10% Pd/C (50 mg), and EtOAc (40 ml) was stirred for 5 h at room temperature under 10 bar of hydrogen. After carefully releasing the hydrogen, the mixture was filtered through a pad of Celite. The filtrate was then evaporated under reduced pressure to give **9ca** as a pale-yellow oil (2.630 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.39 (m, 6H), 2.98 (t, 6H, J=7.8 Hz), 7.33 (dd, 6H, J=8.1 and 2.4 Hz), 7.63 (dd, 6H, J=11.7 and 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.5, 32.5 (t, $^2J_{C-F}$=29.9 Hz), 128.6 (d, $^3J_{C-P}$=12.0 Hz), 131.2 (d, $^1J_{C-P}$=104.8 Hz), 132.6 (d, $^2J_{C-P}$=9.8 Hz), 143.6; ^{31}P NMR ($CDCl_3$, 101 MHz): δ 28.0 (s); Anal. calcd for $C_{42}H_{24}F_{39}PO$: C, 38.32; H, 1.84. Found: C, 38.46; H, 1.52; MS (CI, *m/z*): 1317 (M^++1), 1000, 971, 909, 893, 876.

3.2.15. Tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl]phosphine oxide (9cb). 9cb was prepared from **8cb** in the same way as for **9ca** in 99% isolated yield. Mp 123–125°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (m, 6H), 2.97 (t, 6H, J=7.8 Hz), 7.32 (dd, 6H, J=8.0 and 2.5 Hz), 7.62 (dd, 6H, J=11.6 and 8.0 Hz); ^{31}P NMR ($CDCl_3$, 101 MHz): δ 28.0 (s). Anal. calcd for $C_{48}H_{24}F_{51}PO$: C, 35.66; H, 1.50. Found: C, 35.77; H, 1.28; MS (FAB, *m/z*): 1617 (M^++1), 1247, 1197, 1171, 1093, 1077.

3.2.16. Tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phenyl]phosphine (10ca). A mixture of **9ca** (666 mg, 0.5 mmol), trichlorosilane (339 mg, 2.5 mmol), triethylamine (380 mg, 2.75 mmol), and toluene (10 ml) was stirred at 120°C for 5 h. After cooling to room temperature, saturated $NaHCO_3$ aqueous solution (0.5 ml) was added. The mixture was stirred for 5 min at room temperature, and then filtered through a pad of alumina and washed with toluene (3×15 ml). The filtrate was evaporated under reduced pressure to give **10ca** as a white solid (630 mg, 96%). Mp 69–72°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.37 (m, 6H), 2.92 (m, 6H), 7.19 (d, 6H, J=7.9 Hz), 7.26 (d, 6H, J=7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.6, 33.1 (t, $^2J_{C-F}$=22.1 Hz), 128.9 (d, $^3J_{C-P}$=7.0 Hz), 134.5 (d, $^2J_{C-P}$=19.8 Hz), 135.9 (d, $^1J_{C-P}$=10.8 Hz), 140.3; ^{31}P NMR ($CDCl_3$, 162 MHz): δ −6.8 (s). This compound was first reported by Leitner and Koch.[20d,3b]

3.3. Synthesis of fluoroalkylated BINOLs

3.3.1. (*R*)-6,6′-Bis(1*H*,2*H*-perfluoro-1-octenyl)-2,2′-dibenzyloxy-1,1′-binaphthyl (12a). A solution of (*R*)-6,6′-dibromo-2,2′-dibenzyloxy-1,1′-binaphthyl **11** (1.24 g, 2 mmol), **7a** (1.73 g, 5 mmol), Hermman's palladacycle catalyst (19 mg, 0.02 mmol), and NaOAc (410 mg, 5 mmol) in DMF (10 ml) was stirred for 24 h at 125°C. After cooling to ambient temperature, the solvent was removed under reduced pressure, and the residue was partitioned between EtOAc (50 ml) and water (50 ml). The organic layer was separated, washed with water (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane–EtOAc, 8:1) to give **12a** as a pale-yellow glass-like solid (2.19 g, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.09 (s, 4H), 6.19 (dt, 2H, J_{H-H}=16.2 Hz and J_{F-H}=12.1 Hz), 6.97 (dd, 2H, J=7.4 and 1.7 Hz), 7.05–7.18 (m, 12H), 7.36 (2H, dd, J=8.8 and 1.6 Hz), 7.45 (d, 2H, J=9.1 Hz), 7.92 (s, 2H), 7.96 (d, 2H, J=9.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 71.3, 113.9 (t, J=23.4 Hz), 116.0, 120.6, 124.1, 126.5, 126.9, 127.8, 128.6, 129.4, 129.9, 130.6, 135.3, 137.5, 140.1, 155.7; Anal. calcd

for $C_{50}H_{28}F_{26}O_2$: C 52.02, H 2.44. Found: C 52.41, H 2.18; MS (FAB, *m/z*): 1154 (M^+), 1063, 973, 890, 810; $[\alpha]_D^{10}=-60.8$ (*c* 1.5, $CHCl_3$).

3.3.2. (*R*)-6,6′-Bis(1*H*,2*H*-perfluoro-1-decenyl)-2,2′-dibenzyloxy-1,1′-binaphthyl (12b). 12b was prepared from **11** and **7b** in the same way as for **12a** in 92% isolated yield. Mp 86–88°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.09 (s, 4H), 6.19 (dt, 2H, J_{H-H}=16.0 Hz and J_{F-H}=12.5 Hz), 6.98 (dd, 2H, *J*=7.4 and 1.6 Hz), 7.07–7.18 (m, 12H), 7.36 (dd, 2H, *J*=9.1 and 1.6 Hz), 7.45 (d, 2H, *J*=9.1 Hz), 7.92 (s, 2H), 7.95 (d, 2H, *J*=9.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 71.0, 113.6 (t, *J*=23.5 Hz), 116.4, 120.4, 123.8, 126.3, 126.2, 127.5, 128.3, 129.1, 129.6, 130.3, 135.0, 137.2, 139.8, 155.4; Anal. calcd for $C_{54}H_{28}F_{34}O_2$: C, 47.88; H, 2.08. Found: C, 48.06; H, 1.98; MS (FAB, *m/z*): 1354 (M^+), 1263, 1173, 1139, 910, 819; $[\alpha]_D^{20}=-59.5$ (*c* 1.6, $CHCl_3$).

3.3.3. (*R*)-6,6′-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-2,2′-dihydroxy-1,1′-binaphthyl (13a). A mixture of **12a** (1.73 g, 1.5 mmol), 10% Pd/C (400 mg), and EtOAc (10 ml) was stirred overnight at room temperature under 30 bar of hydrogen. After carefully releasing the hydrogen, the mixture was filtered through a pad of Celite. The filtrate was evaporated under reduced pressure. The resulting residue was purified by flash chromatography (SiO_2, hexane–EtOAc, 2:1) to give **13a** as a pale-yellow oil, which crystallised on standing (1.34 g, 91%). Mp 133–135°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43 (m, 4H), 3.04 (m, 4H), 5.01 (s, 2H), 7.10 (d, 2H, *J*=8.5 Hz), 7.17 (d, 2H, *J*=8.5 and 1.9 Hz), 7.39 (d, 2H, *J*=8.8 Hz), 7.73 (s, 2H), 7.94 (d, 2H, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.7, 33.1 (t, *J*=22.2 Hz), 111.2, 118.6, 125.2, 127.6, 128.6, 130.1, 131.4, 132.6, 135.2, 153.0; Anal. calcd for $C_{36}H_{20}F_{26}O_2$: C 44.19, H 2.06. Found: C 44.58, H 1.85; MS (FAB, *m/z*): 978 (M^+), 632, 489; $[\alpha]_D^{10}=-33.3$ (*c* 1.1, $CHCl_3$).

3.3.4. (*R*)-6,6′-Bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-2,2′-dihydroxy-1,1′-binaphthyl (13b). 13b was prepared from **12b** in the same way as for **13a** in 89% isolated yield. Mp 100–103°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43 (m, 4H), 3.04 (m, 4H), 5.01 (s, 2H), 7.10 (d, 2H, *J*=8.5 Hz), 7.17 (dd, 2H, *J*=8.5 and 1.9 Hz), 7.39 (d, 2H, *J*=8.8 Hz), 7.73 (s, 2H), 7.93 (d, 2H, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.7, 33.1 (t, *J*=22.7 Hz), 111.2, 118.6, 125.2, 127.7, 128.6, 130.0, 131.4, 132.6, 135.2, 153.0; Anal. calcd for $C_{40}H_{20}F_{34}O_2$: C, 40.77; H, 1.71. Found: C, 40.58; H, 1.63; MS (FAB, *m/z*): 1178 (M^+), 745, 736, 732; $[\alpha]_D^{20}=-22.1$ (*c* 1.3, $CHCl_3$).

3.4. Synthesis of fluorous soluble polymer-supported arylphosphines

A solution of 4-(diphenylphosphino)styrene **14** (288 mg, 1 mmol), 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate **15** (4.663 g, 9 mmol), and AIBN (5 mg) in benzotrifluoride (20 ml) was stirred at 65°C for 48 h. Another two portions of AIBN (5 mg) were added in an interval of 16 h. After cooling to room temperature, the solvent was carefully removed under reduced pressure. The residue was suspended in toluene (40 ml) and stirred at 70°C for 20 min, and then cooled with an ice bath. The solid was collected by filtration and washed with toluene (2×20 ml) to give poly[fluoroacrylate-*co*-4-(diphenylphosphino)styrene] **17** as white powder (4.55 g, 92%). The phosphorus content of the polymers was estimated to be 0.8% by ^{31}P NMR using bis(diphenylphosphino)methane as an internal standard. Anal. calcd for $C_{137}H_{80}F_{153}O_{18}P$: C, 33.23; H, 1.63. Found: C, 33.71; H, 1.69; ^{31}P NMR ($C_6H_5CF_3$–$CDCl_3$, 101 MHz): δ −6.2 (s).

The polymer **16** was prepared in a similar way in 93% yield, starting from **14** and **15** with a molar ratio of 1:5. The phosphorus content of the polymers was estimated to be 1.2%. Anal. calcd for $C_{85}H_{52}F_{85}O_{10}P$: C, 35.46; H, 1.82. Found: C, 35.17; H, 1.75; ^{31}P NMR ($C_6H_5CF_3$–$CDCl_3$, 101 MHz): δ −6.2 (s).

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