Phosphorus(III) ligands with fluorous ponytails

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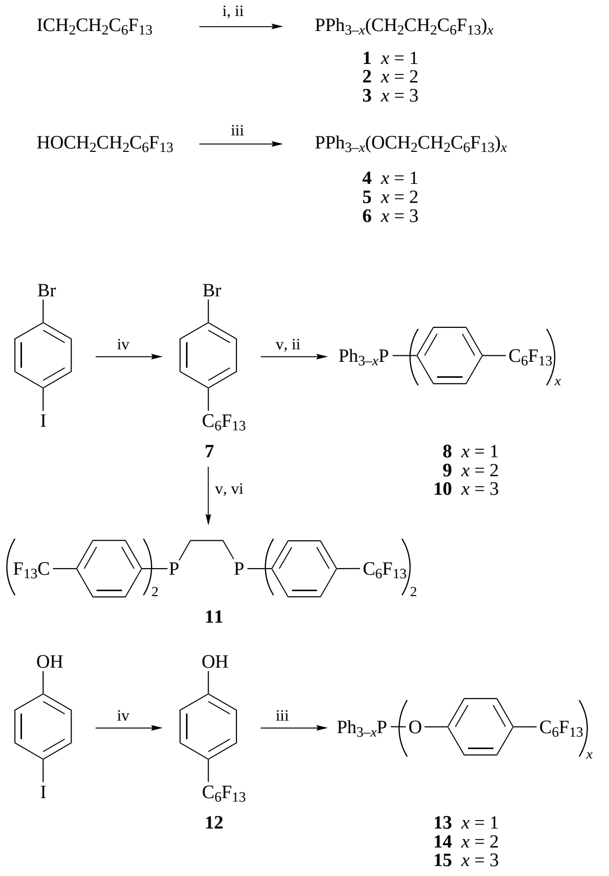
A series of phosphorus(III) compounds incorporating one or more C_6F_{13} 'ponytails' have been prepared as a pool of ligands for coordination and catalytic studies under the fluorous biphase regime. Solubility studies indicate that only ligands with three or more ponytails are preferentially soluble in perfluorocarbon solvents.

Introduction

The commercial exploitation of perfluorinated solvents relies upon their unusual physical and chemical properties such as low miscibilities with common organic solvents, high solubility for gases, particularly oxygen, and low reactivity.[1] A novel application of these properties to the catalyst–product separation problems inherent in homogeneous catalysis has recently been described.[2] In this 'fluorous biphasic (FBS) approach', the catalyst is anchored in the fluorocarbon phase using long perfluorinated side-chains, called 'fluorous ponytails', whereas the substrate(s) and product(s) are dissolved in another solvent (typically an organic solvent). At elevated temperatures the system is homogeneous allowing catalysis to occur, and on cooling the system separates completely allowing the facile separation of the catalyst for recycling. Although the derivatisation of 'established' catalysts with ponytails would appear to offer a straightforward way to exploit this procedure, there have been only a few subsequent applications of this approach in synthetic organic chemistry as a 'fluorous label' for facile substrate–product separation[3] and catalytically in the epoxidation of alkenes.[4] We have a long-standing interest in the synthesis and application of fluorinated organophosphorus ligands[5] and here describe general routes to the preparation of a series of phosphorus(III) ligands containing long perfluorinated groups.

Results and discussion

Scheme 1 illustrates the synthetic rationale for the C_6F_{13} ponytail; analogous chemistry with longer and shorter chain lengths has also been achieved. Only **3** has been reported (incompletely) previously[2] and this new synthetic route, *via* the Grignard reagent, is significantly easier than the route reported previously as it does not require the handling of phosphine (PH_3). Additionally, this route is readily extended to ligands with one or two ponytails (**1** and **2**) offering a general route to a wider range of fluorous derivatised phosphorus(III) ligands. We note that an alternative synthesis of adducts of **1** and **3** has also been reported recently.[6] The direct reaction of the commercially available 1*H*,1*H*,2*H*,2*H*-perfluoro alcohols† with phosphorus chlorides in the presence of base yields a series of related phosphinite **4**, phosphonite **5** and phosphite **6** ligands. For all of these ligands, the C_2H_4 unit has been incorporated to act as a spacer group between the fluorous ponytail and the phosphorus atom in an attempt to minimise the strong electron withdrawing effect of the fluorous tail. The success of this approach can be measured by a comparison of the ^{31}P chemical shifts for these ligands with the analogous molecules with a proton instead of the C_6F_{13} unit (Table 1). For **1**–**3** the introduction of the C_6F_{13} unit causes a small low frequency shift in δ_P whereas in **4**–**6**, the introduction of the same number of ponytails causes a similar magnitude, but high frequency, shift indicating modest success in buffering the influence of the fluorous tails. Ligands **8**–**11** and **13**–**15** contain the alternative C_6H_4 spacer group. The selective copper-mediated coupling reaction of $C_6F_{13}I$ with 4-bromoiodobenzene gives the intermediate **7** in 80% yield.[7] The principal impurity, 1,4-bis(perfluorohexyl)benzene, is readily removed by distillation of the product. Similarly, we find, after appropriate work-up, a 63% yield of the 4-(perfluorohexyl)phenol **12** from the coupling of $C_6F_{13}I$ and 4-iodophenol; a similar coupling reaction using iodoperfluoro ethers has been



Scheme 1 *Reagents and conditions*: i, Mg, Et_2O; ii, $PPh_{3-x}Cl_x$, Et_2O; iii, $PPh_{3-x}Cl_x$, NEt_3, Et_2O; iv, $C_6F_{13}I$, Cu, 2,2′-bipyridine (bipy), DMSO, C_6F_6; v, Bu^nLi, Et_2O; vi, $Cl_2PCH_2CH_2PCl_2$, Et_2O.

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† For the purposes of clarity the nomenclature system used for compounds of this type shows the positions of the hydrogen atoms preceeding the name [*e.g.* **1** (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphine]. The IUPAC system, which has not been used, shows the positions of the *fluorine* substituents [*e.g.* **1** (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)diphenylphosphine].

Table 1 ^{31}P NMR Spectral data for fluorous derivatised ligands[a]

Ligand	C_2H_5[c]	$C_2H_4R_f$[b]	OC_2H_5[c]	$OC_2H_4R_f$[b]	C_6H_5	$C_6H_4R_f$-4[b]	OC_6H_5[d]	$OC_6H_4R_f$-4[b]
PPh_2R	−12.0	−16.0	109.8	116.5	−5.0	−5.0	111.1	112.6
$PPhR_2$	−16.0	−23.0	153.5	156.7	−5.0	−5.4	158.5	159.1
PR_3	−20.4	−25.0	137.1	139.4	−5.0	−6.0	128.2	125.0
$R_2P(CH_2)PR_2$					−12.3	−12.8		

[a] Chemical shifts in ppm. [b] $R_f = C_6F_{13}$. [c] *Handbook of P-31 NMR Data*, CRC Press, Florida, 1991. [d] M. J. Atherton, J. Fawcett, A. P. Hill, J. H. Holloway, E. G. Hope, D. R. Russell, G. C. Saunders and R. M. J. Stead, *J. Chem. Soc., Dalton Trans.*, 1997, 1137.

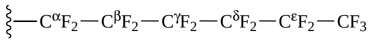

Fig. 1 Atom labelling for fluorous ponytails

described.[8] We were unable to form a Grignard from the intermediate **7** but, after treatment with Bu^{n}Li at low temperature, the addition of the corresponding phosphorus chlorides gave **8**–**11** in high yields. The reaction of the derivatised phenol **12** with the same phosphorus chlorides in the presence of base gave, after work-up, the phosphinite **13**, phosphonite **14** and phosphite **15**. As for the alkyl-substituted ligands above, a comparison of the ^{31}P NMR chemical shifts for these aryl-substituted ligands (Table 1) with those for the parent ligands indicates that the aryl spacers are more effective at reducing the electronic influence of the fluorous ponytails, suggesting that these ligands may have a more extensive coordination chemistry.

The phosphite **6**, is extremely sensitive to hydrolysis, forming $P(OR_f)_2(O)(H)$ (δ_P 7.6, $^1J_{HP}$ 720 Hz), the alkyl-phosphinite and -phosphonite show some hydrolytic sensitivity but **13**–**15** are air- and moisture-stable. The tris-, bis- and mono-arylphosphines show increasing air-sensitivity and the trialkylphosphine **3** undergoes rapid aerial oxidation to $OP(C_2H_4C_6F_{13})_3$ (δ_P 42.6). The solubility of the ligands in perfluorinated solvents increases with the number of ponytails; *i.e.* **1**, **4**, **8** and **13** are slightly soluble in perfluoro-1,3-dimethylcyclohexane whilst **3**, **6**, **10**, **11** and **15** are preferentially soluble in this solvent at room temperature.

The compounds have been characterised by a combination of analytical and spectroscopic techniques. All the compounds show either parent ions $[M^+]$ or $[M + O]^+$ in their mass spectra and fragmentation patterns dominated by loss of fluoride ion, CF_3, C_2F_5 and related fluoroalkyl groups. In the ^1H NMR spectra of **4** and **6**, the chemical shifts of the methylene protons and the $^3J_{HH}$ and $^3J_{HF}$ coupling constants are essentially identical to the values for $C_6F_{13}C_2H_4OH$. Owing to the similar magnitudes of the $^3J_{HH}$ and $^3J_{PH}$ couplings, the OCH_2 resonances in both compounds appear as virtual quartets. For **5**, the OCH_2 and CH_2CF_2 moieties are complicated second-order multiplets. For **4**, **5** and **6** there is no resolvable $^4J_{HP}$ coupling between the CH_2CF_2 protons and the phosphorus nucleus. Likewise, for **10**, the similar magnitude of the $^3J_{HH}$ and $^3J_{HP}$ are responsible for the virtual triplet appearance of the *ortho*-protons. The virtual triplet appearance for the methylene protons in **11** is similar to that for ethylenebis(diphenylphosphine) (dppe).[9] The ^{19}F NMR spectra of **1**–**15** are uninformative and remarkably similar; six, highly consistent, multiplet resonances. The highest frequency resonances are assigned to the terminal CF_3 group. The remaining, CF_2, resonances are assigned according to Fig. 1 from ^{19}F–^{19}F COSY experiments.

This work clearly indicates that a range of phosphorus(III) compounds which are potential ligands for coordination chemistry can be prepared. However, in view of the requirement that three or more ponytails are necessary to confer preferential perfluorocarbon solubility, it is likely that only complexes of these highly derivatised ligands are likely to be useful for catalysis in the FBS. For example, the rhodium–carbonyl chloride complexes of the tris-derivatised ligands **3** and **10** are highly fluorous phase soluble.[10] Further results of our coordination and catalytic studies will be published elsewhere.

Experimental

The ^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker ARX 250 spectrometer at 250.13, 235.34 and 101.26 MHz respectively in $CDCl_3$ unless stated otherwise: all chemical shifts are quoted in ppm using the high frequency positive convention; ^1H NMR spectra were referenced internally or externally to tetramethylsilane, ^{19}F NMR spectra were referenced externally to $CFCl_3$ and ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. Abbreviations for NMR spectral multiplicities are as follows: br = broad, s = singlet, d = doublet, t = triplet, tt = triplet of triplets, dd = doublet of doublets, vt = virtual triplet, vq = virtual quartet, tm = triplet of multiplets, um = unresolved multiplet. Elemental analyses were performed by Butterworth Laboratories Ltd and mass spectra (electron impact and fast atom bombardment in positive mode using 3-nitrobenzyl alcohol matrix) were recorded on a Kratos Concept 1H mass spectrometer.

1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide,† perfluorohexyl iodide and 1*H*,1*H*,2*H*,2*H*-perfluorooctanol (Fluorochem Ltd.) were distilled before use. Diethyl ether was refluxed over sodium metal before use. Triethylamine was dried by distillation from, and stored over, CaH_2. Hexafluorobenzene, perfluoro-1,3-dimethylcyclohexane (F_2 Chemicals Ltd.), DMSO, 4-bromoiodobenzene, 4-iodophenol, phosphorus trichloride, phenyldichlorophosphine, diphenylchlorophosphine and tetrachloro-1,2-diphosphinoethane were used as supplied.

Preparation of phosphorus(III) compounds†

(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)diphenylphosphine 1. A solution of $CF_3(CF_2)_5C_2H_4I$ (23.7 g, 0.05 mmol) in diethyl ether (70 cm^3) was added dropwise to magnesium turnings (1.44 g, 0.06 mol) suspended in diethyl ether (15 cm^3) with two drops of 1,2-dibromoethane. The mixture was refluxed for 2 h, and the solution decanted into a second flask under nitrogen. Diphenylchlorophosphine (11.03 g, 0.05 mol) in diethyl ether (75 cm^3) was added dropwise to the solution over 2 h, and the mixture was hydrolysed with degassed aqueous ammonium chloride. The organic layer was separated, dried over $MgSO_4$ and the solvent removed *in vacuo*. The resulting brown solid was dissolved in the minimum amount of diethyl ether, passed quickly through an alumina column eluting with light petroleum (bp 40–60 °C), the solvent removed *in vacuo* and the white solid heated (60 °C) under dynamic vacuum (0.01 mmHg) for 2 h to remove all traces of fluorinated starting material to leave the product as a white solid, mp 42–44 °C (13.3 g, 50%) (Found: C, 43.0; H, 2.4; F, 48.8. $C_{20}H_{14}F_{13}P$ requires C, 45.1; H, 2.6; F, 46.4%); *m/z* (EI) 532 (M$^+$, 100%), 513 (17) and 185 (60); δ_H 7.0–7.7 (10H, um, C_6H_5), 2.3 (2H, br t, $^3J_{HH}$ 10, PCH_2), 2.1 (2H, um, CH_2CF_2); δ_F −81.3 (3F, t, $^3J_{FF}$ 14, CF_3), −115.0 (2F, um, $C^{\alpha}F_2$), −123.0 (2F, um, $C^{\beta}F_2$), −123.4 (2F, um, $C^{\delta}F_2$), −123.6 (2F, um, $C^{\varepsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phenylphosphine 2. This was prepared similarly using phenyldichlorophosphine (5.513 g, 0.025 mol) affording the product as a white solid, mp 35–37 °C (10 g, 50%) (Found: C, 32.9; H, 1.5; F, 58.4. $C_{22}H_{13}F_{26}P$ requires C, 32.9; H, 1.6; F, 58.7%); *m/z* (EI) 802 (M$^+$, 75%), 783 (29), 733 (5) and 683 (4); δ_H 6.9–7.7 (5H, um, C_6H_5), 2.3 (4H, br t, $^3J_{HH}$ 10, PCH_2), 2.1 (4H, um, CH_2CF_2); δ_F −81.4 (3F, t, $^3J_{FF}$ 12, CF_3), −114.9 (2F, um, $C^{\alpha}F_2$), −122.4 (2F, um, $C^{\beta}F_2$),

−123.4 (2F, um, $C^{\delta}F_2$), −123.7 (2F, um, $C^{\epsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

Tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphine 3. This was prepared similarly using phosphorus trichloride (2.2 g, 0.016 mol) affording the product as a colourless solid–liquid, mp 24–26 °C (8.6 g, 50%) (Found: C, 26.7; H, 1.1; P, 2.5. $C_{24}H_{12}F_{39}P$ requires C, 26.9; H, 1.1; P, 2.9%); *m*/*z* (EI) 1072 (M^+, 86%), 1053 (67), 953 (4), 803 (4), 739 (21) and 656 (46); δ_H 2.3 (6H, br t, $^3J_{HH}$ 10, PCH_2), 2.1 (6H, um, CH_2CF_2); δ_F −81.0 (3F, t, $^3J_{FF}$ 14, CF_3), −114.3 (2F, um, $C^{\alpha}F_2$), −121.7 (2F, um, $C^{\beta}F_2$), −123.0 (2F, um, $C^{\delta}F_2$), −123.7 (2F, um, $C^{\epsilon}F_2$), −126.1 (2F, um, $C^{\gamma}F_2$).

(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl) diphenylphosphinite 4. To a rapidly stirred solution of $CF_3(CF_2)_5C_2H_4OH$ (8.22 g, 22.6 mmol) and trimethylamine (2.3 g, 0.023 mol) in diethyl ether (75 cm^3) was added diphenylchlorophosphine (4.8 g, 21.7 mmol) dropwise over 30 s. Rapid precipitation of $[(C_2H_5)_3NH]Cl$ was accompanied by a mild exotherm, and stirring was continued for a further 10 min. Filtration and concentration of the filtrate *in vacuo* gave the crude compound as a viscous oil. Distillation *in vacuo* using a Kugelröhr apparatus gave the product as a colourless liquid (bp 123–125 °C/1 mmHg) (11.9 g, 85%); [HRMS (EI) Found M^+, 548.05745. $C_{20}H_{14}F_{13}OP$ requires *M*, 548.05747]; δ_H 7.4 (4H, um, *o*-ArH), 7.3 (6H, um, *m*-,*p*-ArH), 4.0 (2H, vq, $^3J_{HH} \sim {}^3J_{PH}$ 7, OCH_2), 2.4 (2H, tt, $^3J_{HH}$ 7, $^3J_{HF}$ 18, CH_2CF_2); δ_F −81.5 (3F, t, $^3J_{FF}$ 12, CF_3), −113.8 (2F, um, $C^{\alpha}F_2$), −122.5 (2F, um, $C^{\beta}F_2$), −123.5 (2F, um, $C^{\delta}F_2$), −124.2 (2F, um, $C^{\epsilon}F_2$), −126.8 (2F, um, $C^{\gamma}F_2$).

Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) phenylphosphonite 5. This was prepared similarly using phenyldichlorophosphine (3.560 g, 0.020 mol) affording the product as a colourless oil (bp 100 °C/0.01 mmHg) (8.998 g, 54%) (Found: C, 31.7; H, 1.5; P, 5.0. $C_{22}H_{13}F_{26}O_2P$ requires C, 31.7; H, 1.6; P, 3.7%); *m*/*z* (EI) 850 ($[M + O]^+$, 20%), 834 (100), 565 (3), 471 (34); δ_H ([$^2H_8$]toluene) 7.3 (2H, um, *o*-ArH), 7.0 (3H, um, *m*-,*p*-ArH), 3.6 (4H, um, OCH_2), 1.8 (4H, um, CH_2CF_2); δ_F([$^2H_8$]toluene) −81.7 (3F, tt, $^3J_{FF}$ 10, $^4J_{FF}$ 2, CF_3), −113.9 (2F, tm, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.3 (2F, um, $C^{\beta}F_2$), −123.3 (2F, um, $C^{\delta}F_2$), −124.1 (2F, um, $C^{\epsilon}F_2$), −126.7 (2F, um, $C^{\gamma}F_2$).

Tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) phosphite 6. This was prepared similarly using phosphorus trichloride (2.2 g, 0.016 mol) affording the product as a colourless liquid (bp 125–130 °C/0.5 mmHg) (8.96 g, 50%) (Found: C, 25.0; H, 0.9; P, 3.8. $C_{24}H_{12}F_{39}O_3P$ requires C, 25.7; H, 1.0; P, 2.8%); *m*/*z* (EI) 1136 ($[M + O]^+$); δ_H 4.0 (6H, vq, $^3J_{HH} \sim {}^3J_{PH}$ 7, OCH_2), 2.4 (6H, tt, $^3J_{HH}$ 7, $^3J_{HF}$ 18, CH_2CF_2); δ_F −81.9 (3F, t, $^3J_{FF}$ 10, CF_3), −114.4 (2F, um, $C^{\alpha}F_2$), −122.7 (2F, um, $C^{\beta}F_2$), −123.7 (2F, um, $C^{\delta}F_2$), −124.5 (2F, um, $C^{\epsilon}F_2$), −127.1 (2F, um, $C^{\gamma}F_2$).

4-(Tridecafluorohexyl)bromobenzene 7. A solution of $C_6F_{13}I$ (18.78 g, 0.042 mol) in hexafluorobenzene (40 cm^3) was added dropwise over 3 h to a stirred mixture of 4-bromoiodobenzene (11.91 g, 0.042 mol), copper powder (5.88 g, 0.092 mol), 2,2′-bipyridine (0.46 g, 2.95×10^{-3} mol), DMSO (40 cm^3) and C_6F_6 (60 cm^3) at 70 °C. The mixture was subsequently stirred at 70 °C for 72 h before it was poured into a beaker containing dichloromethane (100 cm^3) and water (100 cm^3). After filtering, the organic layer was separated, washed with water (3 × 50 cm^3) and dried over $CaCl_2$ and $MgSO_4$. After concentration to 30 cm^3, the crude product was extracted into perfluoro-1,3-dimethylcyclohexane (3 × 20 cm^3) and the solvent removed *in vacuo*. Distillation *in vacuo* using a Kugelröhr apparatus gave the product as a colourless liquid (bp 80–96 °C/0.02 mmHg) (17.0 g, 89%); *m*/*z* (EI) 474/6 ($[M]^+$, 18%), 455/7 (5), 205/7 (100), 126 (30) and 69 (9) (HRMS: Found M^+, 473.928 88. $C_{12}H_4F_{13}{}^{79}Br$ requires *M*, 473.9288); δ_H 7.5 (2H, d, $^3J_{HH}$ 8.5, 3,5-ArH), 7.7 (2H, d, $^3J_{HH}$ 9, 2,6-ArH); δ_F −81.3 (3F, t, $^3J_{FF}$ 10, CF_3), −111.4 (2F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.9 (2F, um, $C^{\beta}F_2$), −122.4 (2F, um, $C^{\delta}F_2$), −123.3 (2F, um, $C^{\epsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

(4-Tridecafluorohexylphenyl)diphenylphosphine 8. *n*-Butyllithium (8.63 cm^3 of 1.6 M solution in hexane) in diethyl ether (25 cm^3) was added dropwise over 1 h to 4-(tridecafluorohexyl)bromobenzene (6.57 g, 0.014 mol) in diethyl ether (75 cm^3) at −78 °C and then stirred at this temperature for a further 1 h. Diphenylchlorophosphine (3.04 g, 0.014 mol) in diethyl ether (25 cm^3) was then added dropwise, at −78 °C, to the reaction mixture over a further hour before the reaction mixture was allowed to warm slowly to room temperature with continuous stirring over a 12 h period. The mixture was hydrolysed with 10% aqueous NH_4Cl (50 cm^3), the organic layer was collected, washed with water (2 × 30 cm^3) and dried over $MgSO_4$. The organic phase was concentrated *in vacuo* to *ca.* 15 cm^3 and passed quickly through an alumina column using 40–60 °C light petroleum as eluent. After the solvent was removed, the white solid was heated in a Kugelröhr oven (80 °C, 0.02 mmHg) to remove starting material, yielding the product as a white solid, mp 76–78 °C (5.3 g, 65%) (Found: C, 49.8; H, 2.2; F, 42.6. $C_{24}H_{14}F_{13}P$ requires C, 49.7; H, 2.4; F, 42.6%); [HRMS (EI) Found M^+, 580.06259. $C_{24}H_{16}F_{13}P$ requires M^+, 580.06256]; *m*/*z* (EI) 580 (M^+, 100%), 311 (3), 241 (1), 203 (23) and 183 (32); δ_H 7.2–7.5 (14H, um, C_6H_5 and C_6H_4); δ_F −81.2 (3F, tt, $^3J_{FF}$ 10, $^4J_{FF}$ 2, CF_3), −111.3 (2F, tm, $^3J_{FF}$ 15, $C^{\alpha}F_2$), −121.9 (2F, um, $C^{\beta}F_2$), −122.2 (2F, um, $C^{\delta}F_2$), −123.2 (2F, um, $C^{\epsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

Bis(4-tridecafluorohexylphenyl)phenylphosphine 9. This was prepared similarly using phenyldichlorophosphine (1.253 g, 7×10^{-3} mol) affording the product as a white solid (3.8 g, 60%) (Found: C, 40.1; H, 1.4; F, 53.4. $C_{30}H_{13}F_{26}P$ requires C, 40.1; H, 1.45; F, 55.0%); *m*/*z* (FAB) 898 (M^+, 100%), 821 (12), 503 (24) and 426 (4); δ_H 7.2–7.6 (13H, um, C_6H_5 and C_6H_4); δ_F −81.3 (3F, t, $^3J_{FF}$ 12, CF_3), −111.4 (2F, um, $C^{\alpha}F_2$), −121.9 (2F, um, $C^{\beta}F_2$), −122.2 (2F, um, $C^{\delta}F_2$), −123.2 (2F, um, $C^{\epsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

Tris(4-tridecafluorohexylphenyl)phosphine 10. This was prepared similarly using phosphorus trichloride (0.64 g, 4.7×10^{-3} mol) affording the product as a white solid, mp 65–67 °C (2.9 g, 50%); *m*/*z* (FAB) 1216 (M^+, 65%), 895 (39), 821 (25), 521 (10) and 252 (30); δ_H 7.5 (6H, d, $^3J_{HH}$ 7, 3,5-ArH), 7.3 (6H, vt, $^3J_{HH} \sim {}^3J_{HP}$ 7, 2,6-ArH); δ_F −81.4 (3F, t, $^3J_{FF}$ 12, CF_3), −111.6 (2F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.0 (2F, um, $C^{\beta}F_2$), −122.3 (2F, um, $C^{\delta}F_2$), −123.4 (2F, um, $C^{\epsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

1,2-Bis[bis(4-tridecafluorohexylphenyl)phosphino]ethane 11. This was prepared similarly using $4\text{-}BrC_6H_4C_6F_{13}$ (7.93 g, 0.017 mol), Bu^nLi (10.4 cm^3, 1.6 M in hexane) and 1,2-bis(dichlorophosphino)ethane (0.97 g, 4.2 mmol) affording the product as a white solid mp 88–90 °C (4.58 g, 66%) (Found: C, 36.6; H, 1.2; F, 57.3. $C_{50}H_{20}F_{52}P_2$ requires C, 36.0; H, 1.2; F, 59.1%); *m*/*z* (FAB) 1703 ($[M + O_2]^+$, 6%), 1687 ($[M + O]^+$, 15), 1671 (M^+, 27), 1291 (12), 955 (17) and 821 (38); δ_H 7.5 (8H, d, $^3J_{HH}$ 9, 3,5-ArH), 7.3 (8H, um, 2,6-ArH), 2.1 (4H, vt, $^3J_{HH} \sim {}^3J_{HP}$ 4, CH_2); δ_F −81.3 (12F, t, $^3J_{FF}$ 10, CF_3), −111.4 (8F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.0 (8F, um, $C^{\beta}F_2$), −122.2 (8F, um, $C^{\delta}F_2$), −123.3 (8F, um, $C^{\epsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

4-Tridecafluorohexylphenol 12. A solution of $C_6F_{13}I$ (48.204 g, 0.108 mol) in hexafluorobenzene (150 cm^3) was added dropwise to a rapidly stirred solution of 4-iodophenol (24.029 g, 0.109 mol), copper (30.825 g, 0.485 mol), 2,2′-bipyridine (1.327 g, 8.5×10^{-3} mol) in DMSO (150 cm^3) over 3 h and the reaction mixture was then heated at 80 °C under nitrogen for 6 days. After cooling to room temperature the mixture was hydrolysed with water, filtered and the filtrate washed with dichloromethane (2 × 100 cm^3). The deep red–brown organic layer was separated, dried over $MgSO_4$ and concentrated to *ca.* 100 cm^3 *in vacuo*. The product was extracted by shaking with perfluoro-1,3-dimethylcyclohexane (8 × 20 cm^3), the washings combined and the solvent removed *in vacuo* to leave an off-white solid. The product was purified by Kugelröhr distillation at 55 °C (0.01 mmHg) to afford **12** as a white crystalline solid (27.977 g, 63%); *m*/*z* (EI) 412 ($[M]^+$, 29%), 393 (10) and 143 (100) (HRMS: Found M^+, 412.01327. $C_{12}H_5F_{13}O$ requires *M*, 412.01328); δ_H 7.3 (2H, d, $^3J_{HH}$ 7.1, 3,5-ArH), 6.9 (2H, d, $^3J_{HH}$ 7.1, 2,6-ArH), 5.2 (1H, s, OH); δ_F −81.3 (3F, tt, $^3J_{FF}$ 10, $^4J_{FF}$ 3,

CF_3), −110.2 (2F, t, $^3J_{FF}$ 15, $C^{\alpha}F_2$), −121.9 (2F, um, $C^{\beta}F_2$), −122.4 (2F, um, $C^{\delta}F_2$), −123.2 (2F, um, $C^{\varepsilon}F_2$), −126.6 (2F, um, $C^{\gamma}F_2$).

4-Tridecafluorohexylphenyl diphenylphosphinite 13. A solution of 4-perfluorohexylphenol (2.236 g, 5.43 mmol) and triethylamine (0.533 g, 5.46 mmol) was added dropwise to a stirred solution of PPh_2Cl (1.082 g, 4.91 mmol) in diethyl ether (50 cm^3) over 1 h. A white precipitate of triethylammonium chloride formed immediately on addition. The reaction mixture was stirred for a further 2 h, filtered through Celite and the solvent removed *in vacuo* to afford the product as a white solid. Unreacted starting materials were removed by heating at 60 °C under vacuum (0.01 mmHg) for 3 h. (1.95 g, 67%) (Found: C, 48.6; H, 2.2; P, 5.2. $C_{24}H_{14}F_{13}OP$ requires C, 48.3; H, 2.4; P, 5.2%); *m*/*z* (EI) 596 (M^+, 82%), 595 (100), 519 (3), 277 (4), 185 (77); δ_H([$^2H_8$]toluene) 7.6 (4H, um, 2,6-ArH), 7.3 (2H, d, $^3J_{HH}$ 9, 3,5-HArR$_f$), 7.15 (6H, um, 3,4,5-ArH), 7.1 (2H, d, $^3J_{HH}$ 9, 2,6-HArR$_f$); δ_F([$^2H_8$]toluene) −81.4 (3F, tt, $^3J_{FF}$ 10, $^4J_{FF}$ 2, CF_3), −109.9 (2F, t, $^3J_{FF}$ 15, $C^{\alpha}F_2$), −121.7 (2F, um, $C^{\beta}F_2$), −122.0 (2F, um, $C^{\delta}F_2$), −123.1 (2F, um, $C^{\varepsilon}F_2$), −126.5 (2F, um, $C^{\gamma}F_2$).

Bis(4-tridecafluorohexylphenyl) phenylphosphonite 14. This was prepared similarly using 4-perfluorohexylphenol (2.704 g, 6.56 mmol), triethylamine (0.670 g, 6.62 mmol) and $PPhCl_2$ (0.541 g, 3.02 mmol) affording the product as a white solid (bp 160 °C/0.01 mmHg) (2.22 g, 79%) (Found: C, 39.8; H, 1.2; F, 51.0; P, 3.4. $C_{30}H_{13}F_{26}O_2P$ requires C, 38.7; H, 1.4; F, 53.1; P, 3.3%); *m*/*z* (EI) 946 ([M + O]$^+$, 100%), 853 (24); δ_H([$^2H_8$]-toluene) 7.8 (2H, um, 2,6-ArH), 7.3 (4H, d, $^3J_{HH}$ 9, 3,5-HArR$_f$), 7.2 (3H, um, 3,4,5-ArH), 7.0 (4H, d, $^3J_{HH}$ 9, 2,6-HArR$_f$); δ_F([$^2H_8$]toluene) −81.5 (3F, tt, $^3J_{FF}$ 10, $^4J_{FF}$ 2, CF_3), −110.4 (2F, t, $^3J_{FF}$ 15, $C^{\alpha}F_2$), −121.7 (2F, um, $C^{\beta}F_2$), −122.2 (2F, um, $C^{\delta}F_2$), −123.1 (2F, um, $C^{\varepsilon}F_2$), −126.5 (2F, um, $C^{\gamma}F_2$).

Tris(4-tridecafluorohexylphenyl) phosphite 15. This was prepared similarly using 4-perfluorohexylphenol (2.64 g, 6.4 mmol), triethylamine (0.81 g, 8 mmol) and phosphorus trichloride (0.27 g, 2 mmol) affording the product as a colourless viscous oil (bp 125 °C/0.01 mmHg) (1.38 g, 55.7%) (Found: C, 34.0; H, 1.15; F, 55.35. $C_{36}H_{12}F_{39}O_3P$ requires C, 34.2; H, 1.0; F, 58.6%); *m*/*z* (EI) 1264 (M^+, 10%), 1263 ([M − H]$^+$, 26), 995 (11) and 853 (81); δ_H 7.2 (6H, d, $^3J_{HH}$ 9, 3,5-ArH), 6.9 (6H, d, $^3J_{HH}$ 9, 2,6-ArH); δ_F −81.4 (9F, tt, $^3J_{FF}$ 10, $^4J_{FF}$ 3, CF_3), −110.5 (6F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.7 (6F, um, $C^{\beta}F_2$), −122.1 (6F, um, $C^{\delta}F_2$), −123.1 (6F, um, $C^{\varepsilon}F_2$), −126.5 (6F, um, $C^{\gamma}F_2$).

Acknowledgements

We would like to thank the EPSRC (P. B., D. G., D. R. P., A. M. S.), BP Chemicals Ltd. (D. R. P.) and the Royal Society (E. G. H.) for financial support.

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Paper 7/04872F
Received 8*th July* 1997
Accepted 22*nd August* 1997