Highly Fluorous Bidentate Phosphines

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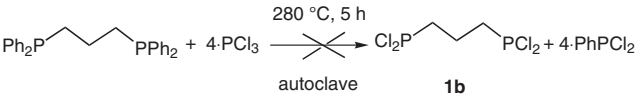
Abstract: The reaction of tetrachlorodiphosphines [$Cl_2P(CH_2)_nPCl_2$; n = 2–4] with fluorous aromatic precursors 4-bromo(perfluorohexyl)benzene and 4-(perfluorohexyl)phenol gave a series of fluorous-tagged diphosphines [(*p*-$C_6F_{13}C_6H_4)_2P(CH_2)_nP(C_6H_4C_6F_{13}$-*p*)$_2$; n = 2–4] and a new diphosphonite [(*p*-$C_6F_{13}C_6H_4O)_2P(CH_2)_3P(OC_6H_4C_6F_{13}$-*p*)$_2$]. The improved synthesis of 1,3-bis(dichlorophosphino)propane (dcpp), involved the facile chlorination of the corresponding primary phosphine with triphosgene. Fluorinated diimines RN=C(CH_3)C(CH_3)=NR, where R = *p*-$C_6H_4C_6F_{13}$ or *p*-$C_6H_4C_8F_{17}$ have also been prepared, and were found to be air-stable alternatives to the highly air-sensitive phosphorus-containing ligands. All compounds were characterised by a variety of techniques including NMR, IR, MS and microanalysis. The successful reduction of the phosphine-oxides [(*p*-$C_6F_{13}C_6H_4)_2P(O)(CH_2)_nP(O)(C_6H_4C_6F_{13}$-*p*)$_2$; n = 2,3] with phenylsilane is also presented.

Key words: fluorous phosphine, $scCO_2$ catalysis, supercritical fluids, copper coupling

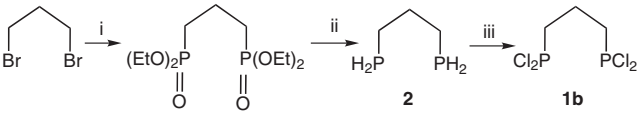
Since Horvath and Rabai's discovery[1] that molecules containing greater than 60% by weight in fluorine will separate into their own 'fluorous phase', there have been copious new applications of fluorinated compounds in synthetic chemistry.[2,3] Molecules with varying degrees of fluorination (i.e. below 60% by weight fluorine) can be separated quite easily on fluorous-reverse-phase-silica-gel (FRPSG).[4] This separation can even be achieved based on the size, shape and number of fluorous tags in a compound.[3] Furthermore, since highly fluorous molecules exhibit excellent solubility in supercritical CO_2 ($scCO_2$), such fluorous molecules have experienced much current interest. In particular, the ability of highly-fluorous catalysts to separate from the organic substrates and reaction mixtures in which they are used, is fundamental to recycling expensive homogeneous catalysts, making this approach to catalysis more attractive to industry.[5]

The synthesis of 1,3-bis(dichlorophosphino)propane (**1b**) has been reported in the literature by Sommer,[6] who claimed that 1,3-bis(diphenylphosphino)propane (dppp) could be chlorinated by phosphorus trichloride at 280 °C in an autoclave (Equation 1).

In our hands, the only identifiable products that were isolated after work-up were $PhPCl_2$ and Ph_2PCl, and problems with this synthesis have been noted by others.[7] We



Equation 1 Attempted synthesis of 1,3-bis(dichlorophosphino)propane (**1b**)



Scheme 1 *Reagents and conditions*: (i) $P(OEt)_3$; (ii) $LiAlH_4$, Et_2O; (iii) triphosgene, CH_2Cl_2.

pursued an alternative approach, which gave **1b** in good yield, by the facile chlorination of 1,3-diphosphinopropane (**2**) with triphosgene (Scheme 1). Triphosgene [$Cl_3COC(O)OCCl_3$] offers a much safer alternative to phosgene for the chlorination of PH units, since it is solid at ambient conditions and can be handled quite easily. A recent review covers the wide range of applications for triphosgene in organic synthesis.[8] Diphosgene has also been used to chlorinate **2**.[9] The synthesis of the primary phosphine **2** was achieved in two steps; Michaelis–Arbusov reaction of 1,3-dibromopropane with triethylphosphite,[10] followed by reduction of the propylene diphosphonate with lithium aluminium hydride (Scheme 1). This method can be employed on scales up to 200 grams. For the chlorination step, it was important to use a non-nucleophilic solvent such as dichloromethane because triphosgene was found to react with diethyl ether to give $Cl_3COCOOEt$.

Reaction of the tetrachlorodiphosphines with a suitable fluorous-tagged aromatic nucleophile would afford our desired ligands. A survey of the literature revealed a number of copper-coupling procedures for the synthesis of fluorous-tagged aryl halides. Lithium–halogen exchange at the aryl-halide moiety would give the desired aromatic nucleophiles. We made a detailed study of the conditions used for the synthesis of the aryl-precursors and made a number of modifications. The synthesis of the fluorinated precursor 4-bromo(perfluorohexyl)benzene (**3**; Equation 2)[11] was achieved using the substantially cheaper benzotrifluoride as an efficient substitute for perfluorinated benzene.

The phenol precursor 4-(perfluorohexyl)phenol could be accessed by a modified copper-coupling procedure reported in the literature.[11] Here we found that a reduction in the

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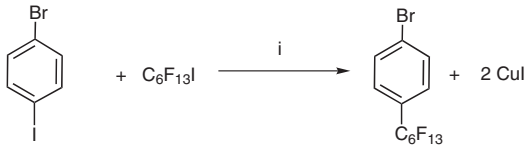
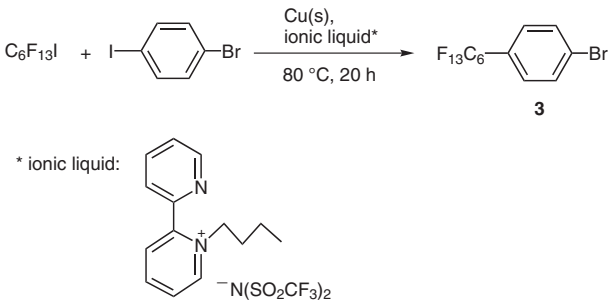
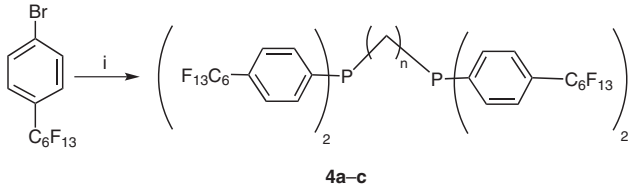


Equation 2 *Reagents and conditions*: (i) Cu, DMSO/$C_6H_5CF_3$, 2,2′-bipyridine, 80 °C, 3 d, under argon.



Equation 3 Copper coupling in an ionic liquid



Equation 4 Synthesis of fluorous diphosphines **4a–c**. *Reagents and conditions*: (i) (a) *n*-BuLi, –78 °C, Et_2O; (b) **1a–c** (0.25 equiv), –78 °C, Et_2O.

number of equivalents of copper used, from 4 to 2.5, and a minor increase (10 °C) in the reaction temperature provided a three-fold quicker reaction time.

In an effort to further improve the efficiency of these copper-coupling reactions, particularly the reaction of 4-bromoiodobenzene with perfluorohexyl iodide, we investigated the use of an ionic liquid as the reaction solvent (Equation 3). The outcome was an appreciably faster reaction compared to the DMSO/$C_6H_5CF_3$ solvent system used previously. This method, however, was only conducted on a small scale as a trial.

Lithiation of **3** with butyllithium followed by quenching with a range of tetrachlorodiphosphines [**1a–c**; n = 2–4), gave the diphosphines dfppe (**4a**; n = 2), dfppp (**4b**; n = 3) and dfppb (**4c**; n = 4), in up to 69% yield (Equation 4).

Although the dfppe analogue **4a** (n = 2) has been reported elsewhere,[11] in our hands the reported procedure gave only the corresponding diphosphine oxide/dioxide. It was found that in solution these ligands were highly sensitive to oxidation and required rigorous Schlenk techniques in order to handle them. However, we were able to regenerate the diphosphines by reduction of the diphosphine oxide/dioxide with phenylsilane ($PhSiH_3$); this procedure is reported in the experimental section.

Table 1 $^{31}P\{^1H\}$ NMR Shifts of Bidentate Phosphines (ppm)

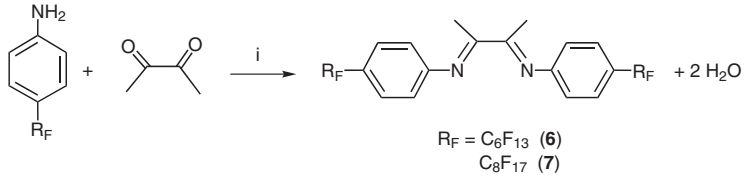
Ligand	R = C_6H_5[19]	R = *p*-$C_6H_4C_6F_{13}$
$R_2P(CH_2)_2PR_2$	–13.2	–12.5
$R_2P(CH_2)_3PR_2$	–17.2	–16.5
$R_2P(CH_2)_4PR_2$	–16.3	–15.3

Based on NMR and mass spectroscopic evidence, we observed an impurity which formed during the syntheses of some of the diphosphines that we believe to be a partially butylated diphosphine arising from reaction of butyllithium with the tetrachlorodiphosphine. This problem was resolved by employing a longer lithium–halogen exchange time.

It should also be noted that during column chromatography of dfppb (**4c**) on alumina the ligand oxidized considerably, even under strict Schlenk conditions.

The reaction of 4-(perfluorohexyl)phenol with a mixture of triethylamine and 1,3-bis(dichlorophosphino)propane (**1b**), gave the diphosphonite dfpop [**5**; *p*-$C_6F_{13}C_6H_4O)_2P(CH_2)_3P(OC_6H_4C_6F_{13}$-*p*)$_2$]. Although a near-quantitative yield was obtained, the diphosphonite was extremely air-sensitive, being susceptible to both oxidation of the phosphorus atoms and hydrolysis of the phosphorus–oxygen bonds.

Given the air-sensitivity of these P(III) ligands compared to their non-fluorous counterparts (e.g. dppe), we sought other potential ligands that would also impart solubility in $scCO_2$. α-Diimine ligands **6** and **7** were targeted due to their good air stability and their application as ligands for palladium-catalysed polyethylene formation.[12–18] The reaction of fluorous anilines with diacetyl gave the α-diimine ligands (Equation 5), albeit in moderate yields. Spectroscopic monitoring (IR and NMR) indicated that the unoptimised reaction proceeded slowly to the final diimine, with a number of intermediate species still observed in the reaction mixture. A low yield for a similar analogue has also been reported.[14]



Equation 5 Synthesis of fluorous diimine ligands (**6**, $R_F = C_6F_{13}$; **7**, $R_F = C_8F_{17}$). *Reagents and conditions*: (i) camphorsulfonic acid (2%), 5 Å MS, benzene, reflux.

Table 1 contains the ^{31}P NMR chemical shifts of the fluorous diphosphines compared with their non-fluorous counterparts. It is clear that the aromatic unit is effective in insulating the phosphorus atoms from the electron-withdrawing power of the C_6F_{13} tails but some effect is still observed. The ^1H NMR spectra for all the diphosphines show common features in the aromatic region whilst the bridging protons exhibit similar multiplicities to those observed for the non-fluorous diphosphine analogues.

In the ^{13}C NMR spectra for all the diphosphines, the C_6F_{13} moieties appear as a series of multiplets over a range of approximately 8 ppm due to the high degree of carbon–fluorine coupling. Ligand mass spectra exhibited signals arising from molecular ions and typical fragmentation patterns.

In conclusion, we have shown that the synthesis of fluorinated diphosphines for potential application in catalysis is not trivial, given the enhanced air-sensitivity of these products over the non-fluorous analogues. However, careful optimisation of the copper-coupling conditions has resulted in significant improvements in overall reaction times and yields compared to established procedures. A number of new ligands have been prepared and their complexation with metal precursors will appear in another publication shortly.

Manipulation of oxygen- and moisture-sensitive materials was carried out under an atmosphere of high purity argon using standard Schlenk techniques or in a dry box equipped with removal columns for H_2O (molecular sieves), O_2 (CuO) and solvent (activated charcoal). NMR (^1H, ^{13}C, ^{31}P and ^{19}F) spectra were acquired on a Bruker AM 300 (^1H at 300.1 MHz, ^{13}C at 75.5 MHz and ^{19}F at 282.4 MHz), Bruker ARX 500 (^1H at 500.1 MHz, ^{13}C at 125.8 MHz, ^{31}P at 202.5 MHz), or Bruker ARX 600 (^1H at 600.1 MHz, ^{13}C at 150.9 MHz, ^{31}P at 242.9 MHz) instruments. ^1H NMR spectra were internally referenced to residual protonated solvent signals, while ^{13}C NMR spectra were internally referenced to the ^{13}C resonance of the deuterated solvent. ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. Chemical shifts (δ) are in parts per million (ppm) and quoted coupling constants (*J*) are given in hertz. Gas chromatography (GC) experiments were performed on a Hewlett Packard 5890 Series II Gas Chromatograph. Infrared spectra were acquired on a Biorad FTS 45 Fourier Transform instrument with a resolution of 2 cm^{-1} unless stated otherwise. Spectra were recorded as KBr discs or Nujol mulls. Mass spectra were recorded on a VG AutoSpec spectrometer operating with an 8 kV accelerating voltage in the FAB^+ (fast atom bombardment – positive ion, using nitrobenzyl alcohol as the matrix), or EI^+ (electron impact – positive ion) mode. Solvent distillations were conducted under an atmosphere of anhydrous, high purity argon. THF and Et_2O were pre-dried over sodium wire and distilled from potassium benzophenone ketyl. Toluene, *n*-hexane and dioxane were pre-dried with sodium wire and distilled from sodium. CH_2Cl_2, cyclohexane and benzotrifluoride were distilled from CaH. Acetone was pre-dried with anhydrous $CaSO_4$ and distilled from this reagent. DMSO was distilled under vacuum and stored over 4Å MS. Diethylamine was distilled from KOH under an atmosphere of argon. PCl_3 was refluxed under argon for 5 h to remove HCl then distilled under argon. 4-Bromoiodobenzene was sublimed under a static vacuum at 50 °C. Perfluorohexyl iodide and perfluorooctyl iodide were distilled under argon; *n*-butyliodide was distilled from $MgSO_4$ under argon and was stored in the dark at –25 °C over Ca metal. 1,2-Bis(dichlorophosphino)ethane (**1a**), *n*-BuLi, 4-iodophenol, 2,2′-bipyridine, lithium bis(trifluoromethylsulfonyl)imide, perfluorohexane, 1,3-dibromopropane and 1,4-dibromobutane were used as received. 1,3-Diphosphinopropane (**2**),[20] 1,4-bis(dichlorophosphino)butane (**1c**)[21] and 1-butyl-2,2′-bipyridinium bis(trifluoromethanesulfonyl)amide[22] were made according to published procedures.

4-Bromo(perfluorohexyl)benzene (3)

Method A: To an 80 °C mixture of 4-bromoiodobenzene (10.0 g, 35 mmol), Cu powder (5.0 g, 79 mmol), 2,2′-bipyridine (0.4 g, 2.5 mmol), $C_6H_5CF_3$ (60 mL) and DMSO (40 mL) was added a solution of $C_6F_{13}I$ (15.8 g, 35 mmol) in $C_6H_5CF_3$ (40 mL) dropwise over 2 h. The mixture was stirred at 80 °C for 72 h then poured into H_2O (100 mL). The mixture was filtered through Celite, the solids washed with $C_6H_5CF_3$ (50 mL), and the filtrate was poured into a separating funnel. The lower $C_6H_5CF_3$ layer was collected and the aqueous layer was back-extracted with additional $C_6H_5CF_3$ (2 × 50 mL). The combined $C_6H_5CF_3$ extracts were then washed with 1M HCl (2 × 50 mL), H_2O (3 × 100 mL), then dried over $MgSO_4$ and filtered. Removal of $C_6H_5CF_3$ on a rotary evaporator afforded a yellow residue (13.5 g, 79%; by GC this contained 70% **3**). This residue was distilled under vacuum using a Kugelrohr apparatus, affording **3**.

Yield: 5.3 g (31%); colourless liquid; bp 70 °C (0.1 mmHg).

^1H NMR (600.1 MHz, $CDCl_3$): δ = 7.7 (d, $^3J_{H–H}$ = 8.4 Hz, 2 H), 7.5 (d, $^3J_{H–H}$ = 8.4 Hz, 2 H).

MS (EI^+): *m*/*z* = 474 $[M]^+$.

Method B: To a mixture of 4-bromoiodobenzene (0.28 g, 1 mmol), activated Cu (64 mg, 1 mmol) and 1-butyl-2,2′-bipyridinium bis(trifluoromethanesulfonyl)amide (2.9 g) was added $C_6F_{13}I$ (0.46 g, 1 mmol). The mixture was stirred at 80 °C for 20 h then cooled to r.t. and the products were extracted away from the brown ionic liquid with Et_2O (4 × 15mL). The Et_2O was removed by rotary evaporation, leaving a cream/brown solid. Upon addition of subsequent Et_2O, this solid separated into its own phase as a yellow liquid. Further removal of Et_2O regenerated the cream/brown solid (0.64 g, 135% mass balance). ^1H NMR analysis of the solid showed it to contain a mixture of 4-bromoiodobenzene, **3** and residual ionic solvent. GC analysis of the solid indicated a ratio of 32% **3** to 68% 4-bromoiodobenzene.

4-(Perfluorohexyl)phenol

To a suspension of 4-iodophenol (2.5 g, 11.4 mmol), Cu powder (1.8 g, 28 mmol) and 2,2′-bipyridine (0.15 g, 1 mmol) in $C_6H_5CF_3$ (75 mL) and DMSO (15 mL) at 90 °C was added, dropwise, a solution of $C_6F_{13}I$ (5.0 g, 11.2 mmol) in $C_6H_5CF_3$ (30 mL) over 2 h. The mixture was stirred at 90 °C for 55 h then poured into H_2O (50 mL). The resulting mixture was filtered through Celite, the solids washed with $C_6H_5CF_3$ (50 mL), and the filtrate poured into a separating funnel. The lower $C_6H_5CF_3$ layer was collected and the aqueous layer was back-extracted with additional $C_6H_5CF_3$ (2 × 50 mL). The combined $C_6H_5CF_3$ extracts were then washed with 1M HCl (50 mL) and H_2O (50 mL), then dried over $MgSO_4$ and filtered. Removal of $C_6H_5CF_3$ on a rotary evaporator afforded a cream solid, which was recrystallised (*n*-hexane–CH_2Cl_2) to give 4-(perfluorohexyl)phenol as a white crystalline solid (2.1 g, 45%). A further 1.8 g (38%) was obtained from the filtrate.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 7.5 (d, $^3J_{H–H}$ = 8 Hz, 2 H), 6.9 (d, $^3J_{H–H}$ = 8 Hz, 2 H), 5.5–5.0 (br, 1 H, OH).

^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –81.4 (t, *J* = 9.0 Hz, 3 F, CF_3), –110.4 (t, *J* = 14 Hz, 2 F, CF_2), –122.1 (m, 2 F, CF_2), –122.6 (m, 2 F, CF_2), –123.5 (m, 2 F, CF_2), –126.8 (m, 2 F, CF_2).

1,3-Bis(dichlorophosphino)propane (dcpp; 1b)

To a solution of 1,3-diphosphinopropane (**2**; 16 g, 148 mmol) in CH_2Cl_2 (500 mL) was added a solution of triphosgene (60 g, 202 mmol) in CH_2Cl_2 (350 mL) dropwise at –30 °C over 2 h. Effluent gases were bubbled through two NaOH (0.5M) traps. The solution was warmed to r.t. with stirring over 12 h, then unreacted triphosgene was removed by filtration. The solvent was removed in vacuo, leaving a cloudy yellow oil, which was fractionally distilled under vacuum in a short path distillation kit, affording **1b**.

Yield: 31g (84%); colourless oil; bp 82–86 °C (1 mmHg).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.5 (m, 4 H, PCH_2), 2.2 (m, 2 H, CH_2).

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 191.1 (s).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 43.0 (dd, $^1J_{C–P}$ = 46 Hz, $^3J_{C–P}$ = 8 Hz, PCH_2), 17.1 (t, $^2J_{C–P}$ = 14 Hz, CH_2).

$(F_{13}C_6C_6H_4)_2P(CH_2)_2P(C_6H_4C_6F_{13})_2$ (dfppe; 4a)

To a solution of **3** (5.2 g, 10.9 mmol) in Et_2O (50 mL) at –78 °C was added *n*-BuLi (1.5M in *n*-hexane, 7.4 mL, 16.7 mmol) over 2 h. The reaction mixture was stirred at –78 °C for 1 h, then 1,2-bis(dichlorophosphino)ethane (**1a**; 0.58 g, 2.5 mmol) in Et_2O (25 mL) was added dropwise over 30 min. The mixture was allowed to warm to r.t. over 12 h, affording a yellow solution above a white precipitate. To this was added 10% NH_4Cl (50 mL, degassed) with stirring and the mixture was then transferred to a Schlenk separating funnel. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the volume was reduced to 15 mL, giving an orange solution, which was then cooled to –25 °C. A white precipitate formed, and the mother liquor was then decanted into another flask. The remaining white solid was dried in vacuo, affording **4a**.

Yield: 2.6 g (54%).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.6 (m, 8 H, H_γ), 7.4 (m, 8 H, H_β), 2.2 (virt. t, *J* = 4.3 Hz, 4 H, CH_2CH_2).

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = –12.5 (s).

MS (FAB$^+$): *m*/*z* = 1670 [M]$^+$.

$(F_{13}C_6C_6H_4)_2P(CH_2)_3P(C_6H_4C_6F_{13})_2$ (dfppp; 4b)

To a solution of **3** (16.1 g, 33.9 mmol) in Et_2O (150 mL) at –78 °C was added *n*-BuLi (1.6M in *n*-hexane, 22.5 mL) in Et_2O (50 mL) over 80 min. The reaction mixture was stirred at –78 °C for 2 h, then a solution of 1,3-bis(dichlorophosphino)propane (**1b**; 2.0 g, 8.26 mmol) in Et_2O (40 mL) was added dropwise over 90 min. The mixture was allowed to warm to r.t. over 12 h, affording a tan solution above a white precipitate. To this was added a solution of aq NH_4Cl (10%, 100 mL, degassed) with stirring. The mixture was transferred to a Schlenk separating funnel, the Et_2O layer separated, and the aqueous layer was extracted with Et_2O (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered and then reduced to half the volume in vacuo. After 12 h at –25 °C a white precipitate formed, which was filtered and washed with Et_2O–cyclohexane (50:50, 2 × 50 mL), then dried in vacuo to give **4b** as a white powder (8 g, 58%). Similar treatment of the filtrate yielded further product (1.6 g, 11%).

^{1}H NMR (500.1 MHz $CDCl_3$): δ = 7.5 (d, $^3J_{H–H}$ = 8 Hz, 8 H, H_γ), 7.4 (virt. t, *J* = 8 Hz, 8 H, H_β), 2.3 (vt, *J* = 8 Hz, 4 H, PCH_2), 1.6 (m, 2 H, CH_2).

^{31}P{^{1}H} NMR (202.5 MHz $CDCl_3$): δ = –16.5 (s).

^{13}C{^{1}H} NMR (125.8 MHz $CDCl_3$): δ = 142.6 (d, $^1J_{P–C}$ = 17 Hz, C_α), 132.7 (d, $^2J_{P–C}$ = 19 Hz, C_β), 129.6 (t, $^2J_{C–F}$ = 24 Hz, C_ω), 126.9 (m, *J* = 7 Hz, C_γ), 119–106 (m, C_6F_{13} tail), 28.9 (t, *J* = 13 Hz, PCH_2), 22.1 (t, *J* = 17 Hz, CH_2).

MS (FAB$^+$): *m*/*z* = 1685 [M]$^+$, 1468 [M – C_4F_9]$^+$, 1289 [M – $C_6H_4C_6F_{13}$]$^+$.

$(F_{13}C_6C_6H_4)_2P(CH_2)_4P(C_6H_4C_6F_{13})_2$ (dfppb; 4c)

To a solution of **3** (4 g, 8.4 mmol) in Et_2O (40 mL) at –78 °C was added *n*-BuLi (1.6M in *n*-hexane, 5.6 mL) over 2 h. The reaction mixture was stirred at –78 °C for 1 h, then 1,4-bis(dichlorophosphino)butane (**1c**; 0.5 g, 1.9 mmol) dissolved in Et_2O–THF (50:50, 70 mL total volume) was added dropwise over 45 min. The mixture was sustained at –78 °C for 2 h, then allowed to warm to r.t. over 12 h. To the brown suspension was added aq sat. NH_4Cl (25 mL, degassed), the organic layer was decanted off and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and filtered [^{31}P NMR of the filtered solution: ^{31}P{^{1}H} NMR (unlocked in the Et_2O–THF mixture): δ = –14.5 (s, 80%, attributed to **4c**), –23.5 (m, 20%, suspected butylated impurity)]. All solvents were removed in vacuo, leaving a brown oil. To this was added toluene (40 mL) and Et_2O (40 mL), which dissolved most of the oil. Addition of MeCN (80 mL) followed by cooling to –25 °C for 12 h gave a brown oil beneath a yellow solution. The supernatant solution was taken and reduced to dryness in vacuo, affording an orange oil (1.3 g, 41%). Integration of the ^{31}P NMR spectrum of this oil showed it to contain **4c** (28%), suspected butylated impurities (51%), and oxidised phosphine materials (21%).

The brown oil that was beneath the supernatant was dissolved in $C_6H_5CF_3$ (10 mL), then subjected to column chromatography on alumina under argon (Et_2O–hexane, 0% then 5%) and the desired fraction was recrystallised (EtOH) to afford **4c**.

Yield: 0.1 g (3%); white powder.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.6 (m, 8 H, H_γ), 7.5 (m, 8 H, H_β), 2.1 (m, 4 H, PCH_2), 1.6 (m, 4 H, CH_2CH_2).

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = –15.3 (s).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 143.0 (d, *J* = 17 Hz, C_α), 132.8 (d, *J* = 19 Hz, C_β), 129.5 (t, *J* = 25 Hz, C_ω), 126.9 (m, C_γ), 121–106 (m, C_6F_{13} tails), 27.2 [m, $P(CH_2)_4P$].

MS (FAB$^+$): *m*/*z* = 1697 [M]$^+$.

Reduction of Phosphine Oxides with Phenylsilane; Typical Procedure

Compound $\{(F_{13}C_6C_6H_4)_2P(O)CH_2\}_2CH_2$ (4.7 g, 2.74 mmol) and neat $PhSiH_3$ (8 mL) were heated at reflux for 48 h. Upon cooling, the translucent mixture formed a white precipitate, which was filtered, washed with cyclohexane (2 × 20 mL) and dried in vacuo to afford a white solid (2.4 g, 50%). Purification was achieved by recrystallisation (Et_2O–cyclohexane) to give a white powder, confirmed as **4b** by ^{31}P and ^{1}H NMR spectroscopy.

$(F_{13}C_6C_6H_4O)_2P(CH_2)_3P(OC_6H_4C_6F_{13})_2$ (dfpop; 5)

To a solution of 1,3-bis(dichlorophosphino)propane (**1b**; 0.14 g, 0.57 mmol) dissolved in Et_2O (10 mL) was added Et_3N (0.35 mL, 2.5 mmol). The reaction mixture was stirred at r.t. for a few minutes, then a solution of 4-(perfluorohexyl)phenol (1 g, 2.4 mmol) in Et_2O (10 mL) was added dropwise over 30 min. The mixture was stirred at r.t. for 2 h then filtered through Celite, which was rinsed with Et_2O (100 mL). The filtrate was reduced to dryness in vacuo to give **5**.

Yield: 0.84 g (84%); pale-yellow oil.

^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.2 (m, 8 H, H_β), 6.8 (m, 8 H, H_γ), 2.0 (m, 2 H, CH_2), 1.8 (m, 4 H, PCH_2).

^{31}P{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 184.2 (s).

$F_{13}C_6C_6H_4N=C(CH_3)C(CH_3)=NC_6H_4C_6F_{13}$ (6)

4-(Perfluorohexyl)aniline (0.2 g, 0.49 mmol), diacetyl (0.02 g, 0.24 mmol), camphorsulfonic acid (5 mg), benzene (50 mL) and 5 Å MS were heated at reflux for 72 h. Volatiles were removed in vacuo, leaving a brown residue, which was dissolved in EtOH (10 mL). Cooling to –25 °C gave a yellow precipitate that was filtered to give **6**.

Yield: 0.016 g (8%).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.6 (d, *J* = 8 Hz, 4 H, H_α), 6.9 (d, *J* = 8 Hz, 4 H, H_β), 2.2 (s, 6 H, CH_3).

^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –77.2 (t, *J* = 10 Hz, 6 F, CF_3), –106.5 (t, *J* = 14 Hz, 4 F, CF_2Ar), –117.9 (br, 4 F, CF_2), –118.3 (br, 4 F, CF_2), –119.2 (br, 4 F, CF_2), –122.6 (br, 4 F, CF_2).

$F_{17}C_8C_6H_4N=C(CH_3)C(CH_3)=NC_6H_4C_8F_{17}$ (7)

4-(Perfluorooctyl)aniline (1.0 g, 1.96 mmol), diacetyl (0.084 g, 0.98 mmol), camphorsulfonic acid (45 mg) and benzene (120 mL) were heated at reflux with an attached Soxhlet extractor containing 5 Å MS, for 72 h. Volatiles were then removed in vacuo, leaving a brown residue to which was added MeOH (100 mL). Heating to boiling point resulted in the formation of a brown solution with a permanently insoluble tan solid. The suspension was cooled to r.t. and filtered to obtain **7** as a tan solid.

Yield: 0.19 g (18%).

^{1}H NMR (500.1 MHz, acetone-d_6): δ = 7.7 (d, *J* = 8 Hz, 4 H, H_α), 7.1 (d, *J* = 8 Hz, 4 H, H_β), 2.2 (s, 6 H, CH_3).

^{13}C{^{1}H} NMR (125.8 MHz, acetone-d_6): δ = 169.3 (s, C=N), 155.7 (s, C_α), 128.8 (t, *J* = 6 Hz, C_γ), 123.8 (m, C_ω), 119.9 (s, C_β), 15.6 (s, CH_3); the fluorous tag was not observed due to the low sample concentration.

MS (FAB$^+$): *m*/*z* = 1073 $[M]^+$, 536 $[M - C_{10}F_{22}]^+$.

IR (nujol): 1682 (C=N) cm^{-1}.

Anal. Calcd for $C_{32}H_{14}F_{34}N_2$: C, 35.84; H, 1.32; N, 2.61. Found: C, 36.14; H, 1.49; N, 2.87.

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