# Synthesis of a Family of Triarylphosphanes with Fluorous Phase Affinity

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A very efficient synthesis of new perfluoro-functionalized triarylphosphanes using an oxygen substituent as the branching point for the introduction of the perfluoro chain has been developed. This approach enabled the introduction of the perfluoro tail at the *para*, *meta*, and *ortho* position, giving highly perfluorinated analogues of triphenylphosphane containing between 54 and 59 wt% fluorine. This methodology has been extended to the synthesis of a perfluoro analogue of 1,2-bis(diphenylphosphanyl)ethane. Fluorous/organic partition coefficients of some of the perfluorophosphanes have been measured, as well as their rates of oxidation.

## Introduction

Homogeneous organometallic catalysis is now a well-used methodology in organic synthesis, mainly due to the high selectivities observed using these procedures, as well as the very mild conditions used. However, one of the drawbacks of this methodology is the need for the separation of the catalyst from the product(s) for its eventual recycling and reuse. This is an important problem when expensive and often toxic metal catalysts are used. In order to solve this problem, various methods for catalyst immobilization using a two-phase system have been developed, such as biphasic system water-organic solvent,[1,2] Supported Aqueous Phase Catalysis (SAPC),[3] Fluorous Biphasic Systems (FBS),[4−12] and ionic liquids.[13−15]

Since the initial reports of Vogt[16] and Ràbaï,[17] there has been an increasing interest in the use of fluorous biphasic systems in catalysis. This technique is based on the temperature-dependent miscibility of perfluorinated and organic solvents and on the use of homogeneous organometallic catalysts that are soluble only in the perfluoro solvent. The reactions can be conducted under monophasic conditions by the appropriate choice of the reaction temperature, and the two phases readily separated at lower temperature, allowing a very easy separation of the two phases. The recovered catalyst can then be easily separated and eventually recycled.

As phosphanes play a pivotal role in organometallic catalysis, it is little wonder that many efforts have been devoted to the synthesis of ligands of this class that are soluble in fluorinated solvents. The introduction of a number of perfluoroalkyl tails of appropriate length into the structure of the phosphane gives perfluorophosphane ligands soluble in fluorinated solvents. However, the presence of a non-fluorinated spacer between the donor atom and the perfluoro substituent is often necessary in order to insulate the phosphorous centre from the electron-withdrawing effects of the perfluoroalkyl group and therefore to maintain the stereoelectronic properties of the phosphane.

Gladysz et al. have reported the synthesis of some fluorinated trialkylphosphanes $[P(CH_2)_m(CF_2)_nCF_3]_3$, (with $m$ = 2, 3, 4, 5, and $n$ = 6, 8, 10) by free-radical chain additions of $PH_3$ to the corresponding alkenes $CF_3(CF_2)_n$-$(CH_2)_{m-2}CH{=}CH_2$.[18−19] Analogous perfluorotrialkylphosphanes were prepared by the reaction of the appropriate Grignard reagents with phosphorous trichloride.[20−24]

Fluorinated analogues of triphenylphosphane have also been reported. The aliphatic fluorocarbon chains could be directly attached to the aromatic ring by lithiation of perfluoroalkylbromobenzene followed by reaction with phosphorus trichloride.[20,22,24] Mono- and bidentate perfluoroarylphosphanes bearing one or more $CH_2$ groups between the phenyl ring and the perfluoro chain have been prepared by Br-Li exchange of the appropriate perfluoroalkylethyl- or methylphenylbromide and reaction with $PCl_{3-n}Ph_n$.[24−27] Van Koten and co-workers have developed a new approach for the preparation of perfluorofunctionalized triarylphosphanes using a *p*-silyl substituent as the branching point.[28,29] More recently, a palladium-catalyzed Heck olefination of haloarylphosphane oxides with perfluoroalkenes, followed by reduction, also afforded perfluoroarylphosphanes in high yields.[30]

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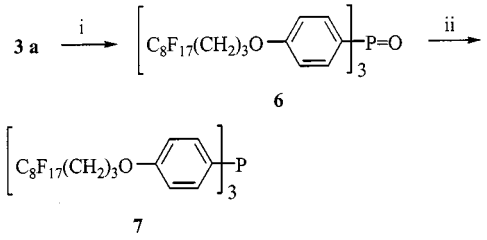
We have previously published a preliminary communication[31] concerning a convenient access to triarylphosphanes with fluorous-phase affinity, where the aliphatic fluorocarbon chain was attached to the aromatic ring by a hydroxyl group. In this paper we present a full account of this approach and its extension to other phosphanes.

## Results and Discussion

The syntheses of two series of perfluoromonophosphanes are shown in Scheme 1 and 2. Tris(4-methoxyphenyl)phosphane (**1a**) and tris(3-methoxyphenyl)phosphane (**1b**) were prepared by reaction of phosphorus trichloride with the Grignard reagent obtained from 4-bromo- and 3-bromoanisole, respectively, as reported by Mann and Chaplin.[32] Tris(2-methoxyphenyl)phosphane (**1c**) was obtained by condensation of 2-methoxyphenyllithium, obtained by *ortho*-lithiation of anisole with BuLi, and $PCl_3$.[33] Bis(4-methoxyphenyl)phenylphosphane (**1d**) was prepared by reaction of the Grignard reagent of 4-bromoanisole with dichlorophenylphosphane.[34] The phosphane oxides **2a**−**d** were obtained in high yields by standard oxidation of the corresponding phosphanes **1a**−**d** with hydrogen peroxide.

Deprotection of the phosphane oxides **2a**−**d** was performed using boron tribromide in dichloromethane,[35] affording the corresponding hydroxyphosphane oxides **3a**−**d** in good yields after recrystallisation.

Coupling of the hydroxyphosphane oxides **3a**−**d** with pentadecafluorooctyl nonafluorobutane sulfonate $C_7F_{15}CH_2OSO_2C_4F_9$, easily obtained by treating pentadecafluorooctanol with a slight excess of $C_4F_9SO_2F$ in diethyl ether in the presence of $Et_3N$,[36] in DMF at 80 °C in the presence of caesium carbonate, provided the fluorinated phosphane oxides **4a**−**d**. Although **4a**−**b** and **4d** were obtained in good yields (59−65%), the *ortho*-substituted phosphane oxide **4c** was obtained in only 13% yield, due probably to steric hindrance. The fluorinated phosphane oxide **6** was obtained in 42% yield by coupling of the hydroxyphosphane oxide **3a** with perfluorooctyl iodide $C_8F_{17}(CH_2)_3I$, obtained according to the literature procedure,[37] under the above conditions.

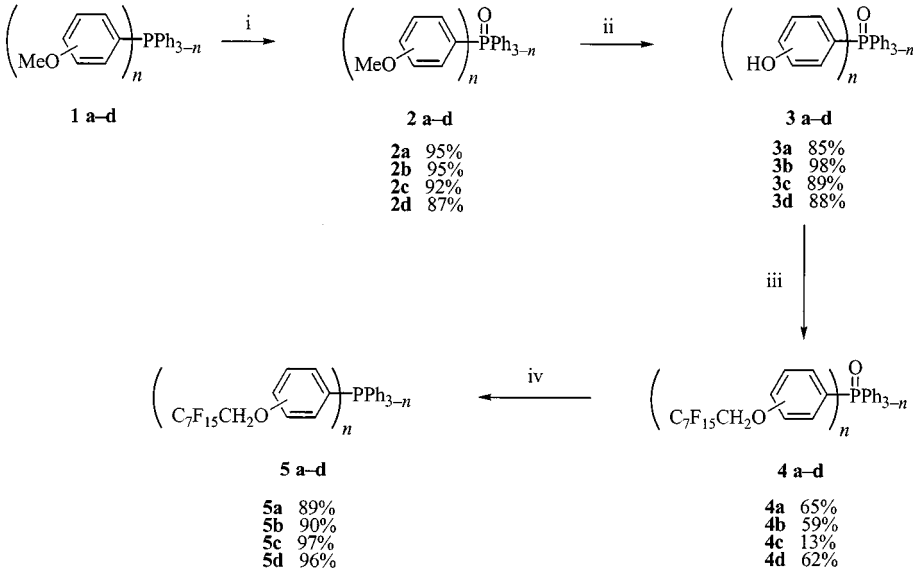



Reagents and conditions: i: $C_8F_{17}(CH_2)_3I$, $Cs_2CO_3$, DMF, 42%; ii: $HSiCl_3$, $Et_3N$, toluene, 92%

Scheme 2. Synthesis of monoperfluorophosphane **7** with a $-(CH_2)_3-$ spacer

The perfluorophosphane oxides **4a**−**d** and **6** were reduced with trichlorosilane in toluene in the presence of triethylamine[38] to give the corresponding perfluorophosphanes **5a**−**d** and **7** in high yields.

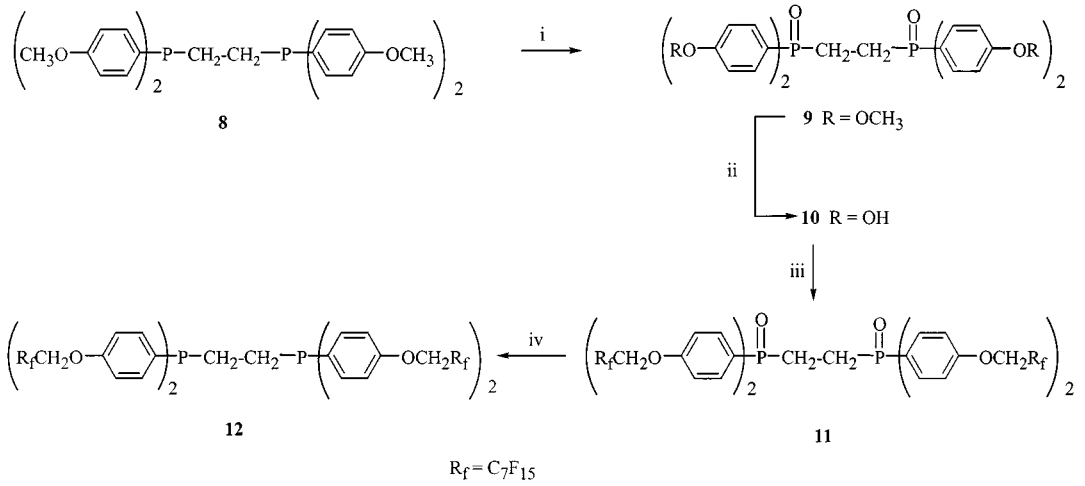
A similar procedure was used to prepare diphosphane **12**, a perfluorinated analogue of 1,2-bis(diphenylphosphanyl)-ethane (Scheme 3). 1,2-Bis[bis(4-methoxyphenyl)phosphanyl]ethane (**8**), obtained by condensation of the Grignard reagent of 4-bromoanisole with 1,2-bis(dichlorophosphanyl)-ethane,[39] was quantitatively oxidized to the diphosphane




**a** : *para* position, $n = 3$; **b** : *meta* position, $n = 3$; **c** : *ortho* position, $n = 3$; **d** : *para* position, $n = 2$

Reagents and conditions: i: $H_2O_2$ 35%; ii: $BBr_3$, $CH_2Cl_2$; iii: $C_7F_{15}CH_2OSO_2C_4F_9$, $Cs_2CO_3$, DMF; iv: $HSiCl_3$, $Et_3N$, toluene

Scheme 1. Synthesis of monoperfluorophosphanes **5a**−**d** with a $-CH_2-$ spacer




Scheme 3. Synthesis of perfluorodiphosphane **12**

oxide **9**. Demethylation of compound **9** with $BBr_3$ afforded the tetrahydroxyphosphane oxide **10** in 92% yield, and condensation of this compound with $C_7F_{15}CH_2OSO_2C_4F_9$ under the above conditions gave the perfluorinated diphosphane oxide **11** in 20% yield after column chromatography; all attempts to optimize this yield failed. Reduction of the diphosphane oxide **11** afforded the perfluorinated diphosphane **12** in 73% yield.

All novel phosphanes were fully characterized by their NMR spectroscopic data and their correct elemental analysis. A comparison of the $^{31}P$ chemical shifts for perfluorophosphane oxides and perfluorophosphanes and their non-perfluorinated analogues (Table 1) indicates only a minor variation. For example, the chemical shifts for phosphanes **1a** and **5a** are at $\delta = -9.7$ and $-9.5$, respectively, and for phosphanes **1c** and **5c** with the substituent at the *ortho* position at $\delta = -35.6$ and $-39.0$, respectively. This indicates that the introduction of a $-CH_2O-$ or a $-(CH_2)_3O-$ spacer is very effective in minimising the strong electron-withdrawing effect of the fluorinated tail on the phosphorus atom. $^{19}F$ NMR spectroscopic data for all these types of perfluorophosphanes and phosphane oxides are very similar.

As we are interested in using these ligands in organometallic catalysis, we measured the solubility of the phosphanes in biphasic solvent combinations. The liquid-liquid partition coefficients $P$ ($P = c_{\text{fluorous phase}}/c_{\text{organic solvent}}$) for the phosphanes **5** between Galden D-100 as the fluorous solvent and various organic solvents are listed in Table 2. Phosphane **5a** has a high partition coefficient in Galden D100/ethanol ($P = 24.6$), as well as in Galden D-100/toluene ($P = 10.4$). On the other hand, THF, acetonitrile and ethyl acetate have low partition coefficients. The *meta*- and *ortho*-substituted perfluorophosphanes **5b** and **5c** have lower partition coefficients than the *para*-substituted analogue in Galden D-100/ethanol ($P = 8.0$ and 7.7, respectively). As expected the partition coefficient of phosphane **5d**, with a lower fluorine content, is lower than that of **5a** ($P = 1.6$).

Table 1. $^{31}P$ NMR chemical shifts for phosphanes and phosphane oxides

| Entry | Compound | δ |
|---|---|---|
| 1 | **2a** | +29.7 |
| 2 | **4a** | +27.9 |
| 3 | **6** | +28.8 |
| 4 | **2b** | +30.2 |
| 5 | **4b** | +28.4 |
| 6 | **2c** | +26.6 |
| 7 | **4c** | +23.5 |
| 8 | **2d** | +29.9 |
| 9 | **4d** | +28.5 |
| 10 | **1a** | −9.7 |
| 11 | **5a** | −9.5 |
| 12 | **7** | −9.6 |
| 13 | **1b** | −2.7 |
| 14 | **5b** | −3.2 |
| 15 | **1c** | −35.6 |
| 16 | **5c** | −39.0 |
| 17 | **1d** | −8.0 |
| 18 | **5d** | −8.1 |
| 19 | **9** | +33.4 |
| 20 | **11** | +32.5 |
| 21 | **8** | −15.7 |
| 22 | **12** | −15.5 |

The *para*-substituted phosphane **7**, with a $-(CH_2)_3-$ spacer instead of a $-CH_2-$ spacer, and therefore a lower fluorine content (% F = 57.3), is high ($P = 18.6$). We also tried to measure the solubility of the perfluorodiphosphane **12** in various perfluorinated and organic solvents. However, the very low solubility of this diphosphane in these solvents did not allow the determination of the partition coefficients; such a behaviour was previously noticed by van Koten et al. in the case of perfluorinated bis(diphenylphosphanyl)-ethane.[29]

In order to study the stability of these phosphanes under catalytic reactions, we studied the rate of oxidation of some

Table 2. Partition coefficients for some perfluorophosphanes

| Compound | F content (wt%) | Organic solvent | $P$[a] |
|---|---|---|---|
| **5a** | 58.7 | $C_2H_5OH$ | 24.6 |
| | | THF | 0.6 |
| | | Toluene | 10.4 |
| | | $CH_3CN$ | 1.1 |
| | | $CH_3CO_2C_2H_5$ | 0.7 |
| **5b** | 58.7 | $C_2H_5OH$ | 8.0 |
| **5c** | 58.7 | $C_2H_5OH$ | 7.7 |
| **5d** | 53.9 | $C_2H_5OH$ | 1.6 |
| **7** | 57.3 | $C_2H_5OH$ | 18.6 |

[a] In a 50:50 (v:v) mixture of Galden D-100/organic solvent at 25 °C

of our perfluorophosphanes **5a**−**d**, using the non-perfluorinated phosphane **1a** as a standard (Figure 1). The perfluorinated phosphane was dissolved in $CDCl_3$ in a Schlenk tube under argon and stirred at room temperature in the air. A sample was taken each hour and analysed by $^{31}P$ NMR spectroscopy. We observed that the oxidation of the perfluorinated phosphanes **5a**−**d** is more difficult than the oxidation of the non-perfluorinated phosphane **1a**. Among the perfluorinated phosphanes, the rate of oxidation of the *ortho*-substituted phosphane **5c** is slower than those of the other perfluorophosphanes **5a**, **5b** and **5d**. These results give an idea of the relative stabilities of the different phosphanes towards oxidation.

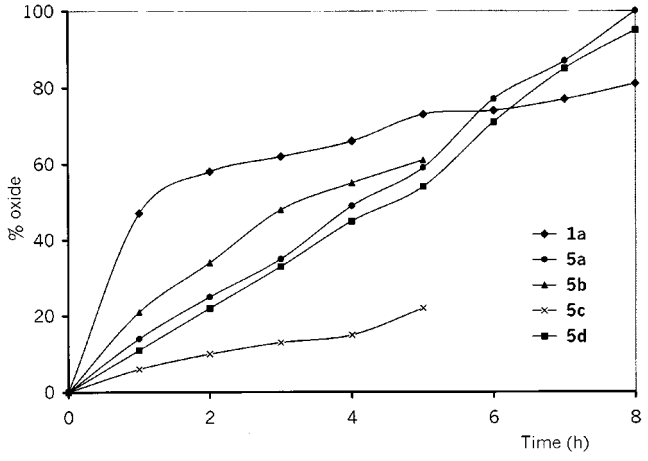



Figure 1. Oxidation of the perfluorophosphanes

## Conclusion

In conclusion we have described a practical and very simple method to synthesize new fluorinated triarylphosphanes bearing one fluorinated tag attached through oxygen as a branching point. Phosphanes containing between 53.9 and 58.7 wt% fluorine are easily accessible with this methodology. These phosphanes generally show high partition coefficients in $C_2H_5OH$ or toluene/perfluorosolvent systems, and are less subject, particularly the *ortho*-substituted perfluorophosphanes, to oxidation than the non-perfluorinated analogues. We are currently using this methodology for the preparation of chiral perfluorophosphanes as well as the use of these achiral ligands in organometallic catalysis.

## Experimental Section

**General Remarks:** Reactions were conducted under a dinitrogen atmosphere unless noted otherwise. $(C_6H_5)PCl_2$, 4-$CH_3OC_6H_4Br$, 3-$CH_3OC_6H_4Br$, 2-$CH_3OC_6H_5$, $PCl_3$, $Cl_2PCH_2CH_2PCl_2$, $C_7F_{15}CH_2OH$, $C_4F_9SO_2F$, $BBr_3$, $Cs_2CO_3$, $HSiCl_3$, were used as received and stored under nitrogen. Galden D-100 (mainly perfluorooctane) was a gift from Ausimont. $(4\text{-}CH_3OC_6H_4)_3P$ (**1a**),[32] $(3\text{-}CH_3OC_6H_4)_3P$ (**1b**),[32] $(2\text{-}CH_3OC_6H_4)_3P$ (**1c**),[33] $C_6H_5(4\text{-}CH_3OC_6H_4)_2P$ (**1d**),[34] $(4\text{-}CH_3OC_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}OCH_3)_2$ (**8**),[39] and $C_8F_{17}(CH_2)_3I$[37] were prepared according to literature procedures.

NMR spectra were recorded with Bruker AM 300 and Avance 300 spectrometers at ambient probe temperature and referenced as follows: $^1H$ (300 MHz), residual $CHCl_3$ at δ = 7.27; $^{13}C$ (75 MHz), internal $CDCl_3$ at δ = 77.23; $^{31}P$ (80 and 121 MHz), external 85% $H_3PO_4$ (δ = 0.00); $^{19}F$ (282 MHz), external $CFCl_3$ (δ = 0.00).

**General Procedure for the Preparation of Methoxyphosphane Oxides 2 and 9:** Water (2 mL) and $H_2O_2$ 35% (9 mmol, 1 mL) were slowly added to a solution of phosphane **1** (8.5 mmol) or **8** (4.25 mmol) in acetone (30 mL). After stirring for 1 h, the acetone was evaporated and $CH_2Cl_2$ (50 mL) was added. The organic phase was washed with a saturated aqueous solution of NaCl (3 × 35 mL), the aqueous solution was extracted with $CH_2Cl_2$ (2 × 25 mL), and the combined organic solutions were dried over $Na_2SO_4$. The solvent was removed on a rotary evaporator to give the methoxyphosphane oxide **2** or **9**.

**Tris(4-methoxyphenyl)phosphane Oxide (2a):** Yield 95%. M.p. 143−144 °C [ref.[34] 143−144 °C].

**Tris(3-methoxyphenyl)phosphane Oxide (2b):** Yield 95%. M.p. 150−152 ($CH_3OH$) °C [ref.[40] 150−152 °C ($CH_3OH$)]

**Tris(2-methoxyphenyl)phosphane Oxide (2c):** White solid. Yield 92%. M.p. 205−206 °C. $^1H$ NMR ($CDCl_3$): δ = 3.55 (s, 9 H, $CH_3$), 6.86−6.99 (m, 6 H, $H_{arom}$), 7.42−7.54 (m, 6 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 55.5 (s), 111.3 (d, $^3J_{C,P}$ = 5.7 Hz), 120.3 (d, $^3J_{C,P}$ = 10.9 Hz), 120.8 (d, $^1J_{C,P}$ = 110.9 Hz), 133.1 (s), 134.4 (d, $^2J_{C,P}$ = 7.9 Hz,), 159.6 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 26.6 (s). $C_{21}H_{21}O_4P$ (368.4): calcd. C 68.47, H 5.75; found C 68.05, H 5.82.

**Phenylbis(4-methoxyphenyl)phosphane Oxide (2d):** Yield 87%. M.p. 95 °C (cyclohexane) [ref.[34] 96−97 °C].

**1,2-Bis[bis(4-methoxyphenyl)phosphanyl]ethane Oxide (9):** White solid. Yield 98%. M.p. 180−181 °C. $^1H$ NMR ($CDCl_3$): δ = 2.40 (t, $^3J_{H,H}$ = 4.0 Hz, 4 H, $CH_2$), 3.80 (s, 12 H, $CH_3$), 6.91 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, $H_{arom}$), 7.57 (dd, $^3J_{H,H}$ = 8.1, $^3J_{H,P}$ = 11.0 Hz, 8 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.2 (d, $^1J_{C,P}$ = 67.8 Hz), 55.4 (s), 114.4 (t, $^3J_{C,P}$ = 6.8 Hz), 123.4 (d, $^1J_{C,P}$ = 108.5 Hz), 132.7 (t, $^2J_{C,P}$ = 4.5 Hz), 162.5 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.4 (s). $C_{30}H_{32}O_6P_2$ (550.5): calcd. C 65.43, H 5.86; found C 65.57, H 5.78.

**General Procedure for the Preparation of Hydroxyphosphane Oxides 3 and 10:** A solution of $BBr_3$ (1 M in $CH_2Cl_2$; 67 mmol, 67 mL) was slowly added at −10 °C to a solution of the methoxyphosphane **2** (13.3 mmol) or **9** (6.65 mmol) in $CH_2Cl_2$ (50 mL) under argon. After being stirred for 20 h at room temperature, the solution was

slowly poured into cold water (200 mL). After partial evaporation of the solvents, the aqueous phase was filtered and extracted with ethyl acetate (3 × 120 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (2 × 12 mL) and dried. Evaporation of the solvent gave the hydroxyphosphane oxide **3** or **10** as a solid which was recrystallised from ethyl acetate for **3a**, water for **3b** and **3c**, and a hexane/ethyl acetate mixture for **3d**.

**Tris(4-hydroxyphenyl)phosphane Oxide (3a):** Yield 85%. M.p. 275−276 °C (ethyl acetate) [ref.[34] 273−275 °C (MeOH)].

**Tris(3-hydroxyphenyl)phosphane Oxide (3b):** Yield 98%. M.p. 270−272 °C (water) [ref.[40] 270−272 °C (water)]

**Tris(2-hydroxyphenyl)phosphane Oxide (3c):** White solid. Yield 89%. M.p. 210−211 °C (water). $^1$H NMR ($CDCl_3$): δ = 6.89−7.06 (m, 9 H, $H_{arom}$), 7.45−7.51 (m, 3 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 112.2 (d, $^1J_{C,P}$ = 106.6 Hz), 119.8 (d, $^3J_{C,P}$ = 7.5 Hz), 120.3 (d, $^3J_{C,P}$ = 12.8 Hz), 132.2 (d, $^2J_{C,P}$ = 10.3 Hz), 135.8 (d, $^4J_{C,P}$ = 1.6 Hz), 162.7 (d, $^2J_{C,P}$ = 3.0 Hz). $^{31}P\{^1H\}$ NMR ([$D_6$]DMSO): δ = 52.3 (s). $C_{18}H_{15}O_4P$ (326.3): calcd. C 66.26, H 4.63; found C 66.09, H 4.67.

**Phenylbis(4-hydroxyphenyl)phosphane Oxide (3d):** Yield 88%. M.p. 232 °C (ethyl acetate) [ref.[34] 233−234 °C (MeOH)].

**1,2-Bis[bis(4-hydroxyphenyl)phosphanyl]ethane Oxide (10):** White solid. Yield 92%. M.p. > 300 °C. $^1$H NMR ($CD_3OD$): δ = 2.36 (br. s, 4 H, $CH_2$), 6.91 (d, $^3J_{H,H}$ = 7.9 Hz, 8 H, $H_{arom}$), 7.44−7.54 (m, 8 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ([$D_6$]DMSO): δ = 45.2 (s), 115.6 (d, $^3J_{C,P}$ = 7.0 Hz), 122.9 (d, $^1J_{C,P}$ = 109 Hz), 132.3 (d, $^2J_{C,P}$ = 4.7 Hz), 160.3 (s). $^{31}P\{^1H\}$ NMR ([$D_6$]DMSO): δ = 35.8 (s).

**2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyl Nonafluorobutanesulfonate:** $C_4F_9SO_2F$ (3.4 g, 11 mmol) was slowly added under argon at 0 °C to a solution of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanol (4 g, 10 mmol) and $NEt_3$ (1.55 mL, 11 mmol) in diethyl ether (20 mL). After being stirred for 24 h at room temperature, the solution was treated with $H_2O$ (10 mL) and diethyl ether (20 mL). The ether layer was separated, washed with brine and dried over sodium sulfate. Evaporation of the solvent afforded 6.2 g of the butaflate as a solid (yield 95%) that was pure enough for further reaction. $^1$H NMR ($CDCl_3$): δ = 4.85 (t, $J_{H,F}$ = 12.1 Hz, $CH_2$), in agreement with the literature data.[36]

**General Procedure for the Preparation of Perfluorinated Phosphane Oxides 4 and 11:** A mixture of hydroxyphosphane oxide (2 mmol for **4**, and 1 mmol for **10**), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl nonafluorobutanesulfonate (5.45 g, 8 mmol), and $Cs_2CO_3$ (1.63 g, 10 mmol) in DMF (25 mL) was stirred at 80 °C under $N_2$ for 18 h. The suspension was then cooled to room temperature and poured into $H_2O$ (30 mL). The aqueous solution was extracted with $Et_2O$ (3 × 50 mL), the combined organic phases were washed with an saturated aqueous solution of NaCl (2 × 50 mL) and dried over $Na_2SO_4$. Evaporation of the solvent gave a residue that was purified by column chromatography (compounds **4a**, **4b**, **4d**, and **11**) or recrystallization from ethanol (compound **4c**).

**Tris[4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)phenyl]phosphane Oxide (4a):** White solid. Yield 65%. $R_f$ = 0.55 (diethyl ether/$CH_2Cl_2$ 1:1). M.p. 103−104 °C. $^1$H NMR ($CDCl_3$): δ = 4.51 (t, $^3J_{H,F}$ = 12.1 Hz, 6 H, $CH_2$), 7.03 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,P}$ = 1.8 Hz, 6 H, $H_{arom}$), 7.62 (dd, $^3J_{H,H}$ = 8.8, $^3J_{H,P}$ = 11.4 Hz, 6 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial): δ = 65.0 (t, $^2J_{C,F}$ = 27 Hz, $CH_2$), 114.9 (d, $^3J_{C,P}$ = 13.6 Hz, $C_{arom}$), 127.1 (d, $^1J_{C,P}$ = 110.2 Hz, $C_{arom}$), 134.1 (d, $^2J_{C,P}$ = 11.6 Hz, $C_{arom}$), 160.1 (s, $C_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.7 (s, 6 F), −123.6 (s, 6 F), −123.3 (s, 6 F), −122.5 (s, 12 F), −119.9 (s, 6 F), −81.3 (t, $^3J_{F,F}$ = 9.5 Hz, 9 F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.9 (s). $C_{42}H_{18}F_{45}O_4P$ (1472.5): calcd. C 34.26, H 1.23; found C 34.96, H 1.36.

**Tris[3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)phenyl]phosphane Oxide (4b):** White solid. Yield 59%. $R_f$ = 0.4 (diethyl ether/$CH_2Cl_2$ 1:9). M.p. 104−105 °C. $^1$H NMR ($CDCl_3$): δ = 4.47 (t, $^3J_{H,F}$ = 12.8 Hz, 6 H, $CH_2$), 7.14−7.33 (m, 9 H, $H_{arom}$), 7.40−7.47 (m, 3 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial): δ = 65.7 (t, $^2J_{C,F}$ = 28 Hz, $CH_2$), 117.9 (s, $C_{arom}$), 120.1 (s, $C_{arom}$), 126.5 (d, $^2J_{C,P}$ = 8.5 Hz, $C_{arom}$), 130.7 (d, $^3J_{C,P}$ = 12.4, $C_{arom}$), 133.8 (d, $^1J_{C,P}$ = 103.6 Hz, $C_{arom}$), 158.0 (d, $^3J_{C,P}$ = 14.1 Hz, $C_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.6 (s, 6 F), −123.5 (s, 6 F), −123.2 (s, 6 F), −122.5 (s, 12 F), −119.9 (s, 6 F), −81.2 (t, $^3J_{F,F}$ = 10 Hz, 9 F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 28.4 (s). $C_{42}H_{18}F_{45}O_4P$ (1472.5): calcd. C 34.26, H 1.23; found C 33.95, H 1.09.

**Tris[2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)phenyl]phosphane Oxide (4c):** White solid. Yield 13%. M.p. 141−142 °C (precipitation with diethyl ether). $^1$H NMR ($CDCl_3$): δ = 4.35 (t, $^3J_{H,F}$ = 13.8 Hz, 6 H, $CH_2$), 6.97−7.01 (m, 3 H, $H_{arom}$), 7.12−7.17 (m, 3 H, $H_{arom}$), 7.50−7.63 (m, 6 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial): δ = 67.5 (t, $^2J_{C,F}$ = 25.5 Hz, $CH_2$), 115.3 (d, $^3J_{C,P}$ = 6.2 Hz, $C_{arom}$), 123.6 (d, $^3J_{C,P}$ = 12.1 Hz, $C_{arom}$), 123.7 (d, $^1J_{C,P}$ = 109.9 Hz, $C_{arom}$), 134.1 (s, $C_{arom}$), 135.1 (d, $^2J_{C,P}$ = 8.4 Hz, $C_{arom}$), 159.7 (s, $C_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.7 (s, 6 F), −124.0 (s, 6 F), −123.4 (s, 6 F), −122.6 (s, 12 F), −120.1 (s, 6 F), −81.4 (t, $^3J_{F,F}$ = 9.2 Hz, 9 F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.5 (s). $C_{42}H_{18}F_{45}O_4P$ (1472.5): calcd. C 34.26, H 1.23; found C 33.56, H 1.14.

**Phenylbis[4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)phenyl]phosphane Oxide (4d):** Colourless oil. Yield 62%. $R_f$ = 0.36 (diethyl ether/$CH_2Cl_2$ 1:1). $^1$H NMR ($CDCl_3$): δ = 4.51 (t, $^3J_{H,F}$ = 12.5 Hz, 4 H, $CH_2$), 7.02 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,P}$ = 1.8 Hz, 4 H, $H_{arom}$), 7.44−7.68 (m, 9 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial): δ = 65.0 (t, $^2J_{C,F}$ = 26.8 Hz, $CH_2$), 114.9 (d, $^3J_{C,P}$ = 13.6 Hz, $C_{arom}$), 126.2 (d, $^1J_{C,P}$ = 109.1 Hz, $C_{arom}$), 128.6 (d, $^3J_{C,P}$ = 12.4 Hz, $C_{arom}$), 132.0 (d, $^2J_{C,P}$ = 10.2 Hz, $C_{arom}$), 133.3 (s, $C_{arom}$), 134.2 (d, $^2J_{C,P}$ = 11.3 Hz, Carom), 160.1 (d, $^4J_{C,P}$ = 2.8 Hz, $C_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.7 (s, 4 F), −123.6 (s, 4 F), −123.3 (s, 4 F), −122.6 (s, 8 F), −119.9 (s, 4 F), −81.4 (t, $^3J_{F,F}$ = 9.6 Hz, 6 F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 28.5 (s). $C_{34}H_{17}F_{30}O_3P$ (1074.4): calcd. C 38.01, H 1.59; found C 38.62, H 2.08.

**1,2-Bis{bis[4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyoxy)phenyl]phosphanyl}ethane Oxide (11):** White solid. Yield 20%. $R_f$ = 0.36 ($CH_2Cl_2$/ $CH_3OH$ 95:5). M.p. 165−166 °C. $^1$H NMR ($CDCl_3$): δ = 2.43 (br. s, 4 H, $CH_2$), 4.48 (t, $^3J_{H,F}$ = 12.7 Hz, 8 H, $CH_2$), 6.99 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, $H_{arom}$), 7.64 (dd, $^3J_{H,H}$ = 8.1, $^3J_{H,P}$ = 10.7 Hz, 8 H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial): δ = 30.1 (s), 65.4 (t, $^3J_{C,F}$ = 27.0 Hz), 115.7 (d, $^3J_{C,P}$ = 7.0 Hz), 127.5 (d, $^1J_{C,P}$ = 117.4 Hz), 133.2 (d, $^2J_{C,P}$ = 4.7 Hz), 160.6 (s). $^{19}$F NMR ($CDCl_3$): δ = −126.6 (s, 8 F), −123.5 (s, 8 F), −123.2 (s, 8 F), −122.4 (s, 16 F), −119.7 (s, 8 F), −81.2 (t, $^3J_{F,F}$ = 9.5 Hz, 12 F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 32.5 (s). $C_{58}H_{28}F_{60}O_6P_2$ (2022.7): calcd. C 34.42, H 1.40; found C 34.87, H 1.74.

**Tris[4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)phenyl]phosphane Oxide (6):** A mixture of hydroxyphosphane oxide **3a** (326 mg, 1 mmol), perfluorooctyl iodide (2.34 mg, 4 mmol), and $Cs_2CO_3$ (1.3 g, 8 mmol) in DMF (15 mL) was stirred at 80 °C under $N_2$ for 18 h. The suspension was then cooled to room temperature and poured into $H_2O$ (20 mL). The aqueous so-

lution was extracted with $Et_2O$ (3 × 30 mL), the combined organic phases were washed with an saturated aqueous solution of NaCl (2 × 30 mL) and dried over $Na_2SO_4$. Evaporation of the solvent gave a residue that was purified by column chromatography using $CH_2Cl_2$/diethyl ether (1:1) as the eluent to give 0.72 g of the phosphane oxide **6** (yield 42%) as a white solid. $R_f$ = 0.31. M.p. 132−133 °C. $^1$H NMR ($CDCl_3$): δ = 2.08−2.17 (m, 6 H, $CH_2$), 2.23−2.38 (m, 6 H, $CH_2$), 4.08 (t, $^3J_{H,F}$ = 5.7 Hz, 6 H, $CH_2$), 6.93 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,P}$ = 2.0 Hz, 6 H, $H_{arom}$), 7.55 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,P}$ = 11.6 Hz, 6 H, $H_{arom}$). $^{13}$C{$^1$H} NMR ($CDCl_3$, partial): δ = 20.5 (s, $CH_2$), 27.9 (t, $^2J_{C,F}$ = 22.1 Hz, $CH_2$), 66.4 (s, $CH_2$), 114.4 (d, $^3J_{C,P}$ = 13.0 Hz, $C_{arom}$), 124.9 (d, $^1J_{C,P}$ = 113.2 Hz, $C_{arom}$), 133.9 (d, $^2J_{C,P}$ = 11.3 Hz, $C_{arom}$), 161.3 (s, $C_{arom}$.) $^{19}$F NMR ($CDCl_3$): δ = −123.6 (s, 6 F), −123.9 (s, 6 F), −123.2 (s, 6 F), −122.4 (s, 18 F), −114.8 (s, 6 F), −81.3 (t, $^3J_{F,F}$ = 9.5 Hz, 9 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 28.8 (s). $C_{51}H_{30}F_{51}O_4P$ (1706.7): calcd. C 35.87, H 1.77; found C 35.97, H 1.73.

**General Procedure for the Preparation of the Perfluorophosphanes 5:** $HSiCl_3$ (832 μL, 8.24 mmol) was cautiously added under argon at room temperature to a mixture of phosphane oxide **4** (2.1 mmol) or **11** (1.05 mmol) and freshly distilled triethylamine (1.24 mL, 8.9 mmol) in dry toluene (15 mL). The mixture was warmed to 130 °C and stirred for 3 h. After being cooled to 5 °C, the solution was treated with precooled deaerated 2 N NaOH (50 mL). The aqueous layer was extracted with deaerated $Et_2O$ (3 × 50 mL), and the combined organic layers were washed with deaerated water (2 × 40 mL) and dried over $Na_2SO_4$. Evaporation of the solvent gave the corresponding perfluorophosphane **5** or **11**.

**Tris[4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)-phenyl]phosphane (5a):** White solid. Yield 89%. M.p. 82−83 °C. $^1$H NMR ($CDCl_3$): δ = 4.46 (t, $^3J_{H,F}$ = 12.9 Hz, 6 H, $CH_2$), 6.93 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,P}$ = 0.7 Hz, 6 H, $H_{arom}$), 7.25 (dd, $^3J_{H,H}$ = 8.8, $^3J_{H,P}$ = 7.0 Hz, 6 H, $H_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.6 (s, 6 F), −123.6 (s, 6 F), −123.2 (s, 6 F), −122.5 (s, 12 F), −119.9 (s, 6 F), −81.3 (t, $^3J_{F,F}$ = 10 Hz, 9 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = −9.5 (s). $C_{42}H_{18}F_{45}O_3P$ (1456.5): calcd. C 34.64, H 1.25; found C 34.93, H 1.38.

**Tris[3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)-phenyl]phosphane (5b):** White solid. Yield 90%. M.p. 90−92 °C. $^1$H NMR ($CDCl_3$): δ = 4.39 (t, $^3J_{H,F}$ = 12.7 Hz, 6 H, $CH_2$), 6.86 (d, $^3J_{H,H}$ = 8.1 Hz, 3 H, $H_{arom}$), 6.92−7.02 (m, 6 H, $H_{arom}$), 7.28−7.35 (m, 3 H, $H_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.7 (s, 6 F), −123.8 (s, 6 F), −123.3 (s, 6 F), −122.6 (s, 12 F), −120.1 (s, 6 F), −81.4 (t, $^3J_{F,F}$ = 7.5 Hz, 9 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = −3.2 (s). HRMS (FAB) calcd. for $C_{42}H_{18}F_{45}O_3P$: 1456.0275; found 1456.0279.

**Tris[2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)-phenyl]phosphane (5c):** White solid. Yield 97%. M.p. 93−95 °C. $^1$H NMR ($CDCl_3$): δ = 4.44 (t, $^3J_{H,F}$ = 12.8 Hz, 6 H, $CH_2$), 6.71−6.75 (m, 3 H, $H_{arom}$), 6.90−6.99 (m, 6 H, $H_{arom}$), 7.32−7.37 (m, 3 H, $H_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.9 (s, 6 F), −124.0 (s, 6 F), −123.5 (s, 6 F), −122.8 (s, 12 F), −120.3 (s, 6 F), −81.5 (t, $^3J_{F,F}$ = 10.1 Hz, 9 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = −39.0 (s). HRMS (FAB) calcd. for $C_{42}H_{18}F_{45}O_3P$: 1456.0275; found 1456.0274.

**Phenylbis[4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)-phenyl]phosphane (5d):** Colourless oil. Yield 96%. $^1$H NMR ($CDCl_3$): δ = 4.48 (t, $^3J_{H,F}$ = 12.8 Hz, 4 H, $CH_2$), 6.94 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H, $H_{arom}$), 7.21−7.37 (m, 9 H, $H_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.7 (s, 4 F), −123.6 (s, 4 F), −123.3 (s, 4 F), −122.6 (s, 8 F), −120.0 (s, 4 F), −81.4 (t, $^3J_{F,F}$ = 9.9 Hz, 6 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = −8.1 (s). HRMS (FAB) calcd. for $C_{34}H_{17}F_{30}O_2P$: 1058.0487; found 1058.0461.

**Tris[4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)phenyl]phosphane (7):** Pale yellow solid. Yield 92%. M.p. 97−98 °C. $^1$H NMR ($CDCl_3$): δ = 2.04−2.16 (m, 6 H, $CH_2$), 2.20−2.40 (m, 6 H, $CH_2$), 4.03 (t, $^3J_{H,F}$ = 5.7 Hz, 6 H, $CH_2$), 6.86 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,P}$ = 1.1 Hz, 6 H, $H_{arom}$), 7.22 (dd, $^3J_{H,H}$ = 8.8, $^3J_{H,P}$ = 7.3 Hz, 6 H, $H_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.6 (s, 6 F), −124.0 (s, 6 F), −123.2 (s, 6 F), −122.4 (s, 18 F), −114.8 (s, 6 F), −81.3 (t, $^3J_{F,F}$ = 9.3 Hz, 9 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = −9.6 (s). $C_{51}H_{30}F_{51}O_3P$ (1690.7): calcd. C 36.23, H 1.79; found C 36.68, H 1.91.

**1,2-Bis{bis[4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyoxy)-phenyl]phosphanyl}ethane (12):** White solid. Yield 73%. M.p. 126−127 °C. $^1$H NMR ($CDCl_3$): δ = 1.98 (br. s, 4 H, $CH_2$), 4.45 (t, $^3J_{H,F}$ = 12.6 Hz, 8 H, $CH_2$), 6.88 (d, $^3J_{H,H}$ = 8.7 Hz, 8 H, $H_{arom}$), 7.24−7.29 (m, 8 H, $H_{arom}$). $^{19}$F NMR ($CDCl_3$): δ = −126.7 (s, 8 F), −123.6 (s, 8 F), −123.3 (s, 8 F), −122.5 (s, 16 F), −119.9 (s, 8 F), −81.3 (t, $^3J_{F,F}$ = 9.6 Hz, 12 F). $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = −15.5 (s). $C_{58}H_{28}F_{60}O_4P_2$ (1990.7): calcd. C 34.99, H 1.42; found C 34.68, H 1.30.

**Determination of Partition Coefficients:** The partition coefficients were determined by dissolving 20 mg of the phosphane in a biphasic system consisting of Galden D-100 (1 mL) and the organic solvent (1 mL). The resulting mixture was stirred at 70 °C for 25 min, then cooled at room temperature. After 30 min, the two phases were separated and the solvents evaporated to dryness. The residues were weighed. In some cases, the organic phase was separated and analysed by ICP-AES on phosphorous.

**Oxidation of the Perfluorophosphanes:** The perfluorinated phosphane was dissolved in $CDCl_3$ in a Schlenk tube under argon and then stirred at room temperature in the air. A sample was taken each hour and analysed by $^{31}$P NMR spectroscopy.

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