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Articles

Synthesis and Properties of a Novel Family of Fluorous Triphenylphosphine Derivatives

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A novel approach to the preparation of perfluorotail-functionalized triarylphosphines using a *p*-silyl substituent as the branching point has been developed. This approach enabled the attachment of between three and nine perfluorotails per phosphorus atom, resulting in the production of highly fluorous tris[*p*-(1H,1H,2H,2H-perfluoroalkylsilyl)aryl]phosphines, $P[C_6H_4\text{-}p\text{-}SiMe_{3-n}(CH_2CH_2C_xF_{2x+1})_n]_3$ ($n = 1, 2, 3$; $x = 6, 8$), containing between 50 and 67 wt % fluorine. ^{31}P NMR studies indicate that the phosphorus atoms, and consequently the σ-donor and π-acceptor properties of these phosphines, are not influenced by the electron-withdrawing perfluoroalkyltails. The fluorous triarylphosphines are readily soluble in fluorous solvents and display fluorous phase preference in several fluorous biphasic systems. The phase partitioning of these fluorous ligands, as well as their donor properties, is discussed in relation to their potential for fluorous biphasic catalyst separation.

Introduction

Since Horváth and Rábai's[1] initial report on using the fluorous biphase concept in catalysis, as an alternative to catalyst immobilization in water,[2] in ionic liquids,[3] on surfaces of macromolecules,[4] or on inorganic supports,[5] this field has experienced a growing scientific and industrial interest.[6] Often, appropriate catalytic reactions for this new immobilization technique involve transition metal phosphine catalysts. Therefore, converting conventional phosphine ligands into fluorous solvent soluble derivatives, while keeping their essential stereoelectronic properties intact, seems to be a key point. The metal complexes derived from these modified ligands are ex-

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Table 1. Fluorous Phosphines Based on Different Hydrocarbon Spacers

R	R_nP–(C$_6$H$_4$)–	R_2P–PR_2
a) $(CH_2)_yC_xF_{2x+1}$	n = 1, 2, 3[a, b, c]	x = 6[d]
	x = 6, 8, 10	y = 2
	y = 2, 3, 4	
b) –(C$_6$H$_4$)–C_xF_{2x+1}	n = 1, 2, 3[b, d, f]	x = 6[b, e]
	x = 6	
c) –(C$_6$H$_4$)–$(CH_2)_2C_xF_{2x+1}$	n = 3[g, h]	x = 6, 8[g]
	x = 6	
d) –(C$_6$H$_4$)–$O(CH_2)_yC_xF_{2x+1}$	n = 3[i]	
	x = 7, 8	
	y = 1,3	

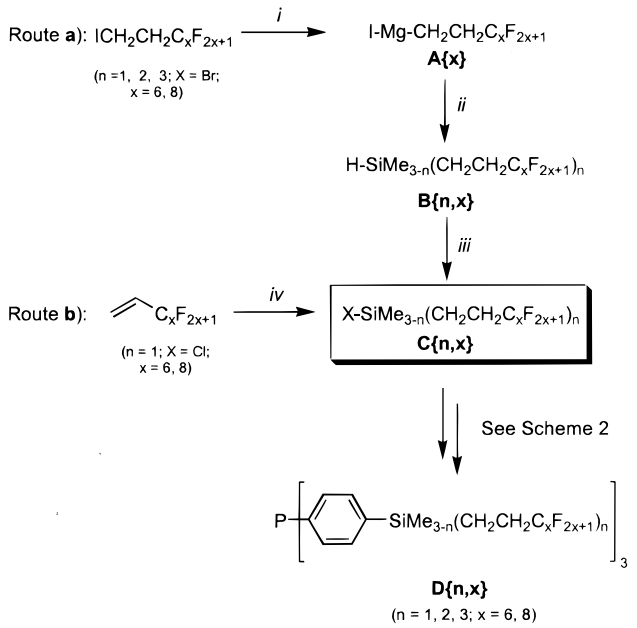
[a] See ref 8b. [b] See ref 8c. [c] See ref 8e. [d] See ref 8a. [e] See ref 8d. [f] See ref 9. [g] See ref 7a. [h] See ref 8f. [i] See ref 12.

pected to be preferentially soluble in apolar perfluorinated solvents, as well as in supercritical carbon dioxide.[7]

Only a limited number of fluorous versions of catalytically important phosphines, such as PPh_3 and R_2PCH_2-CH_2PR_2 (R = alkyl, aryl), have been reported.[8] The most common synthetic approach is the attachment of aliphatic fluorocarbon chains either directly to the phosphorus atom or to the organic substituents of a particular phosphine. However, in all known cases, a nonfluorous spacer group has been necessary to insulate the phosphorus atom from the strongly electron-withdrawing perfluoroalkyltail (Table 1).

In previous studies, either (a) one or more CH_2 groups, (b) an aryl ring, or (c) both have been used as spacer,[7a,b,8,9] leading to fluorous alkyl and aryl phosphines that have also been referred to as "pony" or "pigtail" phosphines. In addition, reports of a number of aryl phosphines with perfluoroalkyl and perfluoroalkyl ether chains containing aromatic C−F bonds have been published.[10] Because these bonds are known to be easily activated by late transition metal complexes,[11] these ligands appear to be less suitable for catalysis. More recently, fluorinated alkoxy groups (d) have been used to increase the solubility of triarylphosphines in fluorous solvents.[12] The observed catalytic activities of fluorous phase soluble catalysts derived from the phosphines in Scheme 1 are generally an order of magnitude lower than those of their nonfluorous analogues.[13]

Scheme 1[a]



[a] Reagents and conditions: (i) 30-fold excess of Mg, diethyl ether, 25 °C; (ii) $HSi(Me)_{3-n}Cl_n$, Et_2O; (iii) Br_2, *n*-hexane (n = 1, 2), *n*-hexane/FC-72 (n = 3), 25 °C; (iv) 1.5 $HSiMe_2Cl$, H_2PtCl_6(aq), reflux.

Inspired by our work on dendrimeric structures containing silicon branching points[4] and work by Curran et al.[14] on the use of fluorous silyl tags and fluorous tin hydrides in organic synthesis, we became interested in developing aryl phosphine ligands with *p*-$SiMe_2CH_2CH_2$ spacer groups (Figure 1). We anticipated that the silicon would provide a positive inductive effect to the aromatic system, in that way neutralizing the electron-withdrawing effect of the perfluoro chain. Furthermore the successive substitution of methyl for $(CH_2)_2C_xF_{2x+1}$ (x = 6, 8) groups allows the attachment of up to nine perfluoroalkyl chains per P atom for a homoleptic triarylphosphine (Figure 1), which is expected to lead to a reduction in

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(13) (a) For example, in the case of olefin hydroformylation, the activity of the Rh/P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ system is ca. 10 times less than that of Rh/PPh_3.[1c] In hydrogenation reactions employing similar catalysts, 16−1073 turnovers in 24 h[13b] and 88−108 turnovers in 8 h[13c] have been observed, which are modest compared to, e.g., Wilkinson's catalyst $RhCl(PPh_3)_3$ (150−600 turnovers/h).[13d] The positive effect of using triarylphosphines instead of trialkylphosphines is well-known in catalytic hydrogenation[13e,f] and has been attributed to the lower basicity of triarylphosphines. Hence, for optimum activity, fluorous triarylphosphines with steric and electronic properties that are closely comparable to those of PPh_3 would be highly desirable. (b) Haar, C. M.; Huang, J.; Nolan, S. P.; Petersen, J. L. *Organometallics* **1998**, *17*, 5018. (c) Rutherford, D.; Juliette, J. J. J.; Rocaboy, C.; Horváth, I. T.; Gladysz, J. A. *Catal. Today* **1998**, *42*, 381. (d) Derived from data in: Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (e) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Boston, MA, 1994; pp 8−9. (f) Montelatici, S.; van der Ent, A.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1054.

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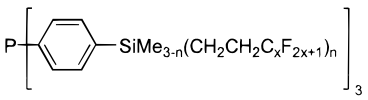

D{n,x}

(n = 1, 2, 3; x = 6, 8)

Figure 1. Fluorous triphenylphosphines with various degrees of fluorous character through the use of silicon as a branching point.

ligand and/or catalyst leaching during fluorous biphasic separation.

In our previous work on fluorous triphenylphosphines **D**{**1,*x***} (x = 6, 8) and in their successful application to the recycling of highly active rhodium-based hydrogenation catalysts by fluorous biphase separation,[15] we obtained indications that fluorous phosphines with higher fluorine content could be advantageous, because recycling of the intact catalyst was limited by the loss of free phosphine (8 and 2% per cycle, respectively). Here, we present (i) a full report on the preparation of fluorous triarylphosphines **D**{**1,*x***}; (ii) a new, versatile synthetic route for the synthesis of higher substituted fluorous triarylphosphines **D**{***n*,*x***} (n = 2, 3) involving the use of a *p*-Si(Me)$_{3-n}$[(CH$_2$)$_2$]$_n$ spacer (n = 1, 2, 3); and (iii) a study on the solubility of the new phosphines in organic and fluorous solvents and their partition coefficients in fluorous biphasic solvent systems.

Results and Discussion

Synthesis. Scheme 1 gives an overview of the two routes used to obtain fluorous silanes **C**{***n*,*x***}, which serve as precursors for the preparation of phosphines **D**{***n*,*x***}. Here n signifies the number of fluorotails per silicon atom, whereas x represents the number of carbons in the C$_x$F$_{2x+1}$ fluorotail. The synthesis of the fluorous phosphines **D**{***n*,*x***} starts from either (1H,1H,2H,2H-perfluoro-1-alkyl)dimethylchlorosilanes **C**{**1,*x***}[15] or bis- and tris(1H,1H,2H,2H-perfluoro-1-alkyl)bromosilanes **C**{***n*,*x***} (n = 2, 3; x = 6, 8; Scheme 1). The silanes **C**{**1,*x***} are commercially available but can also be obtained through hydrosilylation of 1H,1H,2H-perfluoro-1-octene or -decene (step iv, Scheme 1;[16] Table 2, entries 1 and 5). The internal olefins *trans*-Me(H)C=CF(C$_y$F$_{2y+1}$) (y = 5, 7) were obtained as side products (21−40%) and are responsible for the rather moderate yield of the hydrosilylation step. Most likely they are formed by the decomposition of the unstable Markovnikov addition product.[17]

The route via the Grignard reagents of the 1H,1H,-2H,2H-perfluoro-1-alkyl iodides (**A**{***x***}) and reaction with chlorosilanes HSi(Me)$_{3-x}$Cl$_x$ (Scheme 1, route a), which was reported previously for **B**{**3,*x***} (x = 6, 10),[18] has been used to synthesize a six-member library of fluorous alkylsilanes **B**{***n*,*x***} (n = 1, 2, 3; x = 6, 8), with compounds **B**{**2,*x***} and **B**{**3,8**} as the new derivatives. This route also allows more efficient access to silanes **B**{**1,*x***} than provided by hydrosilylation followed by reduction with LiAlH$_4$ (68% compared to 55% yield, x = 6; Table 2, entry 2).[16,19]

Table 2. Yields Obtained in the Synthesis of Fluorous Silanes According to the Methods Used in Scheme 1

entry	{*n*,*x*}	method	**B**{***n*,*x***}[a]	**C**{***n*,*x***}[b]	total yield (%)[c]
1	{1,6}	b	−	60 (63)[d]	60
2	{1,6}	a	68	nd	nd
3	{2,6}	a	79	99	78
4	{3,6}	a	78 (70)[e]	80 (99)[f]	62
5	{1,8}	b	−	79 (66)[d]	79
6	{2,8}	a	70	80	56
7	{3,8}	a	75	92	69

[a] Based on C$_x$F$_{2x+1}$C$_2$H$_4$I, yield of Grignard reaction included. [b] Based on C$_x$F$_{2x+1}$CH=CH$_2$ (n = 1) or **B**{***n*,*x***} (n = 2, 3). [c] Based on C$_x$F$_{2x+1}$CH=CH$_2$ (n = 1) or C$_x$F$_{2x+1}$C$_2$H$_4$I (n = 2, 3). [d] See ref 16. [e] See ref 18a. [f] See ref 18b.

The reactions with dichloromethylsilane and trichlorosilane were straightforward and yielded the fluoroalkylsilanes **B**{***n*,*x***} as air-stable and easy-to-handle materials. Bromination of **B**{***n*,*x***}, following modified literature procedures for **C**{**3,*x***} (x = 6, 10),[18b,c] afforded bromosilanes **C**{***n*,*x***}. An overview of the yields of each step in Scheme 1 is given in Table 2.

Two general strategies for the synthesis of the fluorous aryl phosphines have been followed, specifically, route a, the reaction of lithiated *p*-(fluoroalkylsilyl)bromobenzene **E**{***n*,*x***} with PCl$_3$ or P(OMe)$_3$, and route b, the reaction of fluoroalkylhalosilanes **C**{***n*,*x***} (n = 1, 2, 3) with lithiated tris(*p*-bromophenyl)phosphine (Scheme 2). To be able to compare the effect of the fluoroalkylsilyl substituents with that of a regular methyl group, the known trimethylsilyl derivative **D**{**0**}[20] was prepared as well, following the same synthetic procedure.

Route a (Scheme 2). Silyl chlorides **C**{**1,*x***} were reacted with *p*-bromophenyllithium, which was obtained by lithiation of 1,4-bromoiodobenzene or (less expensive) 1,4-dibromobenzene using an improved literature procedure.[21] The yields of aryl derivatives **E**{***n*,*x***} are listed in Table 3. Colorless liquid **E**{**1,6**} and white, waxy solid **E**{**1,8**} are soluble in benzene, chloroform, and hexane. Minor amounts of 1,4-[SiMe$_2$(CH$_2$)$_2$C$_x$F$_{2x+1}$]$_2$C$_6$H$_4$ (x = 6, 8) were formed as side products. A similar side product has been reported in the copper(I)-mediated coupling reaction of CF$_3$(CF$_2$)$_5$I with *p*-bromoiodobenzene.[8d] The route to **E**{**1,*x***} has also been used in our laboratory for the synthesis of fluorous [NiCl{2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_2$-4-

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(19) The polyfluoroalkyl iodides exhibit a high tendency to form Wurtz-coupling products in the Grignard reaction, especially at temperatures above 25 °C and at concentrations ≥0.4 M. However, the amount of radical dimer could be kept below 10% by performing the Grignard reaction slowly (15 h) at room temperature and at ≤0.22 M concentrations in Et$_2$O.

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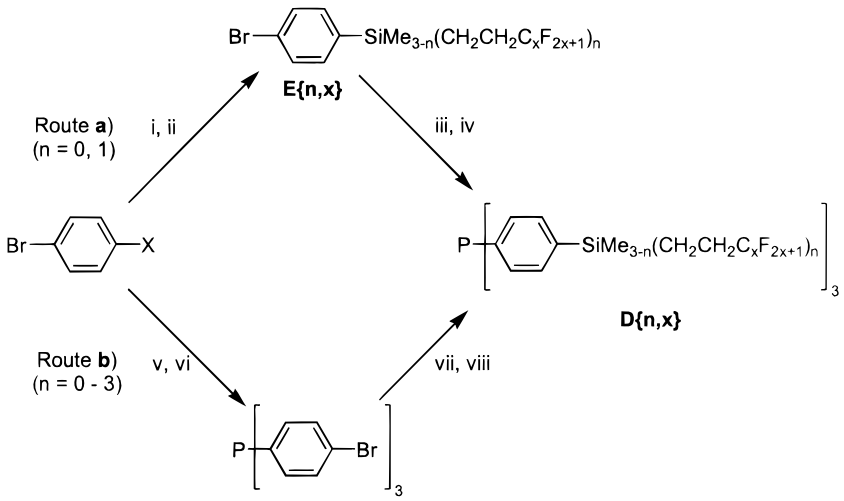
Scheme 2[a]



[a] Reagents and conditions: (i) X = I, ^{n}BuLi, *n*-hexane/*n*-pentane, 0 °C; (ii) **C**{***n,x***}, THF/*n*-pentane, −78 °C then room temperature; (iii) 2 ^{t}BuLi, *n*-hexane, −78 °C then room temperature, or ^{n}BuLi, *n*-hexane, 0 °C then room temperature; (iv) $^1/_3$ PCl_3 or $^1/_3$ $P(OMe)_3$, *n*-hexane/THF, −78 °C then room temperature; (v) X = Br, ^{n}BuLi, *n*-hexane/Et_2O, room temperature; (vi) $^1/_3$ PCl_3, *n*-hexane/Et_2O, −78 °C then room temperature; (vii) 6 ^{t}BuLi, Et_2O/hexane, −78 °C; (viii) 3 **C**{***n,x***}, Et_2O/*n*-hexane, −78 °C then room temperature.

Table 3. Yields Obtained in the Synthesis of Nonfluorous and Fluorous Compounds E and D According to Methods a and b in Scheme 2

entry	method	{*n*,*x*}	**E**{***n,x***}[a] (%)	**D**{***n,x***}[b] (%)
1a	a[c,e]	{0}	98	75
1b	a[d,f]	{0}	98	40
2	b	{0}	–	98
3	a[c,f]	{1,6}	83	62
4	b	{1,6)	–	77
5	b	{2,6}	–	98
6	b	{3,6}	–	86
7a	a[c,e]	{1,8}	87	48
7b	a[d,f]	{1,8}	87	41
8	b	{2,8}	–	90
9	b	{3,8}	–	88

[a] Based on **C**{***n,x***}. [b] Yield based on **E**{**0**}, **E**{**1,*x***} (route a), **C**{**0**}, or **C**{***n,x***} (route b). [c] Using ^{t}BuLi in step ii. [d] Using ^{n}BuLi in step ii. [e] Using $P(OMe)_3$ in step iii. [f] Using PCl_3 in step iii.

$SiMe_2(CH_2)_2(CF_2)_5CF_3$}], a model catalyst for the selective 1:1 Kharasch addition of CCl_4 to methyl methacrylate under fluorous conditions.[22]

Compounds **E**{**1,*x***} were easily lithiated using either ^{t}BuLi (1:2 molar ratio) or ^{n}BuLi (1:1 molar ratio). The fact that the yields were lower than expected is the result of incomplete lithiation rather than side reactions (^{1}H NMR). Lithiation using ^{n}BuLi instead of ^{t}BuLi afforded similar yields, but proved to be more time-consuming. Metathesis of lithiated **E**{**1,*x***} with PCl_3 or $P(OMe)_3$ at 0 °C afforded the desired phosphine ligands **D**{**1,*x***} in moderate overall yields (Table 4).

Route b (Scheme 2). After several unsuccessful attempts to lithiate aryl bromides **E**{***n,x***} bearing more than one fluorotail ($n > 1$), we decided to introduce the fluoroalkylsilyl group by reaction with lithiated tris(*p*-bromophenyl)phosphine. The latter was synthesized in 71% yield by optimization of a literature procedure.[23] The 3-fold lithiation of tris(*p*-bromophenyl)phosphine in diethyl ether is fast and essentially quantitative. Treatment with silanes **C**{***n,x***} ($n = 2$, 3) afforded the phosphines **D**{***n,x***} ($n = 2$, 3) in high yields (86−98%, Table 3). Phosphines **D**{**1,*x***} can also be synthesized more efficiently following this procedure.

Table 4. Overall Yields of Aryl Phosphines D Based on the Different Starting Materials Used

entry	method	{*n*,*x*}	**C**{***n,x***} (%)	PCl_3 (%)	$P(OMe)_3$ (%)	*p*-BrC_6H_4X (%)
1a	a[a]	{0}	75	–	90	68 (X = I)
1b	a[b]	{0}	40	58	–	36 (X = I)
2	b	{0}	98	70	–	70 (X = Br)
3	a[a]	{1,6}	51	68	–	46 (X = I)
4	b	{1,6}	77	55	–	55 (X = Br)
5	b	{2,6}	98	64	–	64 (X = Br)
6	b	{3,6}	88	61	–	61 (X = Br)
7a	a[a]	{1,8}	42	–	65	38 (X = I)
7b	a[b]	{1,8}	35	57	–	35 (X = I)
8	b	{2,8}	90[c]	71	–	71 (X = Br)
9	b	{3,8}	88[c]	69	–	70 (X = Br)

[a] Using ^{t}BuLi in step ii. [b] Using ^{n}BuLi in step ii. [c] Using a 10% excess of **C**{***n,x***}.

The advantage of using route b rather than route a with respect to the use of different starting materials, especially **C**{***n,x***} and *p*-BrC_6H_4X (X = Br, I), becomes clear in a comparison of the overall yields of the phosphines (Table 4). The synthesis of tris[*p*-(trimethylsilyl)-phenyl]phosphine (**D**{**0**}) by method b is nearly quantitative with respect to silane (entry 2), in contrast to the initially reported value (35−45%).[20]

All novel derivatives **B**−**E** were characterized by their NMR spectroscopic data [^{1}H, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P (for phosphines **D**)] and, in several cases, by their correct elemental analyses (**B**{**2,8**}, **B**{**3,8**}, **C**{**2,8**}, **D**{***n,x***}; $n = 1$, 2, 3; $x = 6$, 8).

Interestingly, the silanes **B**{***n*,6**} and halosilanes **C**-{***n*,6**} ($n = 1$, 2, 3) are colorless oils, whereas extending the perfluoro chain by two CF_2 units ($x = 8$) results in waxy solids for $n = 2$ and 3. Boiling and melting points of **C**{***n,x***} increase in order of increasing *n* ($0 < 1 < 2 < 3$) (Table 5). Remarkably, the opposite trend is observed for the fluorous aryl phosphines **D**{***n,x***}, with the excep-

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Table 5. Boiling and Melting Points of Compounds C and D

		C{*n,x*}		D{*n,x*}
entry	{*n,x*}	mp (°C)	bp (°C) (pressure (mbar))	mp (°C)
1	{0}	–	51.0 (10^3)	194 (lit. 187–189)[b]
2	{1,6}	–	76–80 (33)[a]	89
3	{2,6}	–	105 (0.1)	67
4	{3,6}	–	180 (0.1)	50–55
5	{1,8}	–	106–108 (33)[a]	101
6	{2,8}	55	–	72
7	{3,8}	93	–	123–125

[a] See ref 15b. [b] See ref 21.

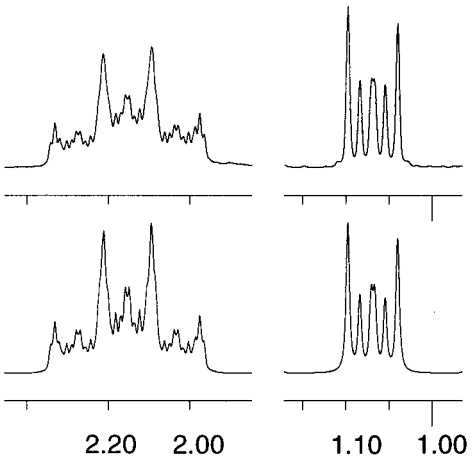

Figure 2. Experimental (top) and simulated (bottom) part of the ^{1}H NMR spectrum of $C_8F_{17}(CH_2)_2Si(Me)_2Cl$ (**C{1,8}**). Simulation parameters: δ_A, 1.07; δ_B, 2.18; coupling constants (Hz), $^2J_{A,A'} = {}^2J_{B,B'} = -15.3$, $^3J_{A,B} = 4.28$, $^3J_{A,B'} = 13.1$, $^4J_{A,X} = 0.36$, $^3J_{B,X} = 18.0$, $^5J_{A,Y} = 0.18$, $^4J_{B,Y} = 1.56$, $^6J_{A,Z} = 0.08$, $^5J_{B,Z} = 0.50$.

tion of **D{3,8}**, which has a melting point higher than those of all other phosphines **D{*n,x*}** (Table 5). Clearly, for **D{*n,x*}**, the introduction of more or longer fluoroalkyl chains results in a decrease in the melting point despite the increase in molecular weight.

The methylene protons of the $-CH_2CH_2Si-$ spacer group in compounds **B**, **C**, **D**, and **E** ($n > 0$) reveal second-order behavior in their ^{1}H NMR spectra, which, in the case of one or three fluorotails per silicon atom ($n = 1$, 3), can be interpreted as the AA′BB′ part of an AA′BB′$X_2Y_2Z_2$ spin system with characteristic $^3J_{H,F}$ values (18 Hz)[24] and long-range couplings up to $^5J_{H,F}$ (Figure 2). In the case of compounds **B{*n,x*}** ($n = 1$, 3), this pattern became visible only on selective decoupling of the CH_2Si-*H* signal.

The sizes of the observed vicinal $^3J_{AB}$ (13.1 Hz) and $^3J_{AB}$ (4.3 Hz) coupling constants are in good agreement with the time-averaged contributions calculated for the three possible rotamers (13.7 and 4.6 Hz, respectively), taking into account the influence of the inductive effect of the silicon and CF_2 substituents on the $J_{H,H}$ coupling constants.[25] The absence of significant changes in the spectra of **C{1,8}** upon cooling to 238 K and warming to 343 K, except for small changes in line width, also corresponds to a fast exchange between the three rotamers (Figure 3).

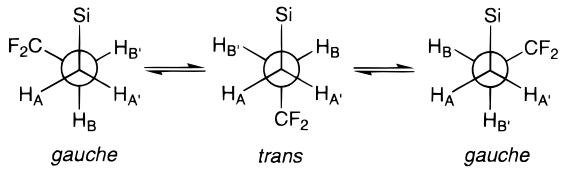

Figure 3. Equilibrium of the three rotational isomers of **B{*n,x*}**, **C{*n,x*}**, **D{*n,x*}**, and **E{*n,x*}** ($n = 1$, 3).

Table 6. Assignment of the ^{19}F[a] and ^{13}C[b] NMR Signals of the 1H,1H,2H,2H-Perfluorooctyl Chain in D{1,6}

	δ ^{19}F	δ ^{13}C [ppm]	spin-spin coupling constants [Hz]
H_2C	-	5.62	$^1J_{C,H} = 121$
CH_2	-	26.6 (t)	$^2J_{C,F} = 23.5$, $^1J_{C,H} = 125$
α-F_2C	-115.8 (qm)	119.3 (tt)	$^1J_{C,F} = -254$, $^2J_{C,F} = 30.5$, $^3J_{H,F} = 17.5$, $^4J_{F\alpha,F\gamma} \sim 15$
β-CF_2	-123.3 (m)	112.3 (tquin)	$^1J_{C,F} = -268$, $^2J_{C,F} = 32.0$, $^4J_{F,F}$ not resolved
γ-F_2C	-122.2 (m)	112.1 (tquin)	$^1J_{C,F} = -271$, $^2J_{C,F} = 31.8$, $^4J_{F\gamma,F\varepsilon} \sim 14$
δ-CF_2	-123.2 (m)	111.3 (tquin)	$^1J_{C,F} = -272$, $^2J_{C,F} = 31.7$, $^4J_{F,F}$ not resolved
ε-F_2C	-126.5 (m)	109.4 (tm)	$^1J_{C,F} = -260$, $^2J_{C,F}$ not resolved, $^4J_{F\gamma,F\varepsilon} \sim 14$
CF_3	-81.4 (tt)	118.1 (qt)	$^1J_{C,F} = -287$, $^2J_{C,F} = 33.3$, $^3J_{F,F} = 2.2$, $^4J_{F,F} = 9.8$

[a] 282.4 MHz, C_6D_6, $T = 25$ °C. [b] 75.5 MHz, C_6D_6, $T = 25$ °C.

For compounds **B{2,*x*}**, **C{2,*x*}**, **D{2,*x*}**, and **E{2,*x*}**, the methylene protons are diastereotopic, which gives rise to more complicated ABCD$X_2Y_2Z_2$ spin systems in which the chemical shifts and the $J_{H,H}$ and $J_{H,F}$ spin–spin coupling constants are different for each methylene proton.

As is demonstrated for **D{1,6}** in Table 6, the complete assignment of the ^{19}F resonances of **D{*n*,6}** with respect to the position of the fluorine atoms in the perfluoroalkyl-tail was made on the basis of literature information[26] and data from several NMR experiments (^{13}C–^{19}F HETCOR, ^{13}C-{^{1}H}, ^{13}C{^{19}F}, ^{19}F COSY, ^{19}F selective decoupling) and differs from that presented in some recent publications.[8c,9,16] C–F correlations were made on the basis of a ^{13}C–^{19}F HETCOR experiment. The CF_3, α-CF_2, and ϵ-CF_2 group resonances in the ^{13}C{^{1}H} spectrum were assigned by their characteristic multiplicities. The signal of the ϵ-CF_2 group was observed as a triplet of multiplets due to $^1J_{C,F}$ and slightly different $^2J_{C,F}$ couplings to CF_3 and δ-CF_2 groups, respectively. This assignment was confirmed by selective ^{19}F decoupling of all CF_2 groups, resulting in a single ^{19}F-coupled signal of the ϵ-CF_2 group in the ^{13}C-{^{19}F} spectrum (quartet due to $^2J_{C,F}$ coupling with CF_3). A ^{19}F–^{19}F COSY experiment, combined with the information from a ^{13}C–^{19}F HETCOR spectrum, allowed the assignment of the remaining ^{13}C and ^{19}F signals, taking into account the well-known phenomenon that $^4J_{F,F} \gg {}^3J_{F,F}$ for freely rotating fluorous aliphatic chains (~10 and ~0 Hz, respectively).[26] Also, these assignments were confirmed by selective ^{19}F decoupling experiments.

In the case of the longer C_8F_{17} chain, the ^{19}F resonances of the two additional CF_2 moieties are not resolved from the γ-fluorine signals. However, the ^{13}C{^{19}F} NMR spectra exhibit two new signals (at δ 111.8 and 111.7 for **D{1,8}** in C_6D_6).

The ^{29}Si NMR spectra of phosphines **D{*n,x*}** clearly show a deshielding of the silicon atom with an increasing

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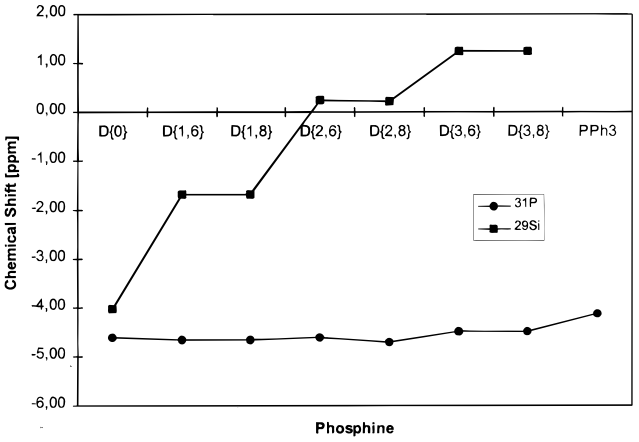

Figure 4. ^{31}P and ^{29}Si chemical shifts for the new fluorous phosphine ligands **D**{***n,x***} and nonfluorous **D**{**0**} and PPh_3. Conditions: $^{31}P\{^1H\}$ NMR, 121.5 MHz; $^{29}Si\{^1H\}$ NMR, 59.6 MHz; solvent, C_6D_6/C_6F_6, 1:1 (v/v); T = 25 °C.

Table 7. Solubilities[a] and Fluorous Partition Coefficients *P*[b] of the Fluorous Aryl Phosphines

compd	F content (wt %)	*n*-octane mol/L	*n*-octane g/L	*c*-$C_6F_{11}CF_3$ mol/L	*c*-$C_6F_{11}CF_3$ g/L	P^c	P^d	P^e
D{1,6}	50	0.037	55	0.050	74	0.26	1.1	1.5
D{1,8}	55	0.008	14	0.055	98	2.2	4.6	2.2
D{2,6}	60	0.005	12	0.249	615	7.8	17	5.7
D{2,8}	63	0.001	3	0.277	851	7.8	28	9.2
D{3,6}	64	–[f]	–[f]	0.162	502	4.3	9.4	15
D{3,8}	67	0.7×10^{-3}	3	0.029	127	2.1	12	20

[a] Expressed as the amount of phosphine that dissolves in 1 L of pure solvent at 25 °C. [b] In a 50:50 (v/v) mixture of *c*-$C_6F_{11}CF_3$/organic solvent ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$) at 0 °C. Derived from an analysis of each of the two phases on phosphorus by ICP–AAS, assuming that the densities of the two phases are those of the pure solvents. The estimated experimental error is less than ±1 in the last digit. [c] *c*-$C_6F_{11}CF_3$/toluene, T_c = 89 °C, where T_c is defined as the critical temperature of the biphasic solvent system. See, for example, ref 27. [d] *c*-$C_6F_{11}CF_3$/*n*-octane, T_c = 42 °C. [e] *c*-$C_6F_{11}CF_3$/*n*-pentane, $T_c \sim$ 10 °C. [f] Formation of a gel.

number of fluorotails, whereas an increase in the length of the fluorotails (x = 6 and 8, respectively) has little effect (Figure 4). The opposite trend was observed for the chemical shift changes of the ^{13}C signals of the CH_2Si and CH_3Si moieties. However, a comparison of the ^{31}P NMR data of compounds **D**{***n,x***}, **D**{**0**}, and PPh_3 indicates clearly that the $-SiMe_{3-n}(CH_2CH_2)_n-$ linker is effective in insulating the phosphorus atom from the electron-withdrawing perfluoroalkyltails. In fact, by comparison with the NMR data for **D**{**0**}, it can be concluded that the observed chemical shift differences between PPh_3 and **D**{***n,x***} are predominantly due to the *p*-silyl substitution (Figure 4).

Solubility and Phase Distribution Studies. As our primary objective for the perfluorotail functionalization of aryl phosphines is to use them as ligands for immobilization of phosphine-based homogeneous catalysts in fluorous solvents,[15] we were interested in the solubility of fluorous aryl phosphines **D** in different solvents and in biphasic solvent combinations. The solubilities of the phosphines **D** in organic and fluorous solvents are listed in Table 7. It appears that the "like dissolves like" principle is valid: The fluorous phosphines have consistently higher solubilities in the fluorous solvent *c*-$C_6F_{11}CF_3$ than in nonfluorous *n*-octane. Remarkably, an optimum in the fluorocarbon solubility is observed for n = 2 (0.25–0.28 mol/L). For n = 3, the solubility drops to values below 0.17 mol/L. The progressive decrease in fluorocarbon solubility with increasing x (6 > 8 > 10) reported for fluorous trialkyl derivatives $P(CH_2CH_2C_xF_{2x+1})_3$[8e] is in contrast to the order 6 < 8 observed for **D**{***n,x***} (n = 1 or 2). However, the reverse order (6 > 8) was observed for n = 3. It is noteworthy that the solubility of fluorous aryl phosphines **D**{**1,*x***} in diethyl ether is significantly higher than the solubilities in *n*-octane, *n*-pentane, and *c*-$C_6F_{11}CF_3$. For example, a >1.0 M diethyl ether solution of **D**{**1,6**} can be prepared, whereas a saturated *n*-pentane solution is ca. 0.16 M. In comparison with **D**{**0**}, the fluorotail-containing phosphines **D**{**1,*x***} (x = 6, 8) display increased *n*-pentane solubility: At a value of ca. 0.22 mol/L, the solubility of **D**{**1,8**} in *n*-pentane is more than twice that of **D**{**0**} (<0.10 mol/L). These observations clearly indicate that the fluorous character of **D**{**1,*x***} is not yet very pronounced, in contrast to that of the higher derivatives **D**-{**2,*x***} and **D**{**3,*x***}.

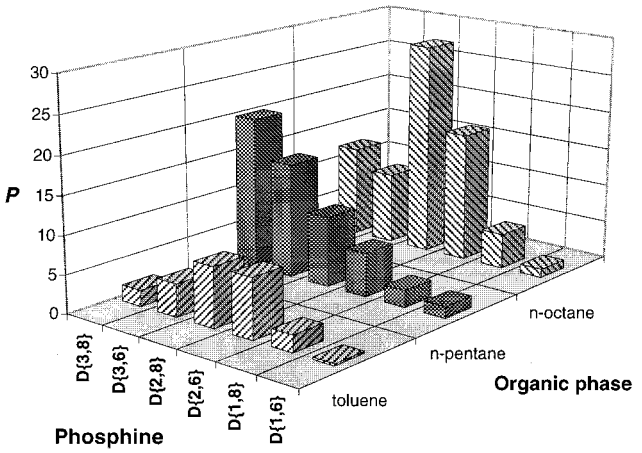

Figure 5. Plot of partition coefficients P ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$) for phosphines **D**{***n,x***} in several fluorous biphasic solvent systems with *c*-$C_6F_{11}CF_3$ as the fluorous phase at 0 °C.

For applications in fluorous biphasic catalysis and for catalyst recycling by fluorous extraction techniques, the most important feature of the fluorous aryl phosphines and derived catalytic complexes is the partition coefficient P ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$) in fluorous biphasic systems. Partition coefficients of the fluorous aryl phosphines were determined in several fluorous biphasic solvent combinations (Table 7 and Figure 5) and reflect the same trend as their solubility data, i.e., there is an optimum for **D**{**2,6**} and **D**{**2,8**}, except for *c*-$C_6F_{11}CF_3$/*n*-pentane for which, presumably because of the lower critical temperature (T_c) of ca. 10 °C, a steady increase of P with the weight percent of fluorine was found, with a peak at **D**{**3,8**}. The best fluorous phase affinity was found for **D**{**2,8**} in *c*-$C_6F_{11}CF_3$/*n*-octane (P = 28).

In comparison with fluorous trialkylphosphines $P(CH_2CH_2C_8F_{17})_3$ (P = 332 in *c*-$C_6F_{11}CF_3$/toluene),[1c,8e] relatively small partition coefficients were found for our fluorotail-bearing aryl phosphine ligands (cf. P = 2.2 for **D**{**1,8**}). Consequently, there is not a simple relation between P and the weight percent of F in the phosphine; undoubtedly, there is also an effect of the partial degree of aromatic character, i.e., the number of aryl groups in the phosphine (Figure 5).

Despite the relatively small fluorous phase affinity of the fluorous phosphine **D**{**1,*x***}, we have been able to demonstrate that rhodium leaching for RhCl[**D**{**1,*x***}]$_3$ in hydrogenation catalysis can be as low as 0.1%.[15e] Because of their higher partition coefficients, fluorous phosphines **D**{***n*,*x***} with $n > 1$, especially with $n = 2$, are even more interesting for further reduction of Rh and phosphine leaching in fluorous biphasic catalyst separation.

Conclusions

We have demonstrated straightforward synthetic routes for the synthesis of novel, highly fluorous triarylphosphines, which are of interest for fluorous phase catalysis and catalyst recovery by fluorous biphasic extraction. By using silicon as a branching point, it became possible to attach between three and nine perfluorotails per phosphorus atom. Through this method, phosphines containing between 50 and 67 wt % fluorine were prepared, which reveal distinct fluorous phase affinity in fluorous biphasic solvent systems and good solubility in fluorous solvents. ^{31}P NMR studies confirm the effective insulation of the phosphorus atom, and consequently its donor properties, from the electron-withdrawing effect of the perfluorotails. Surprisingly, the fluorous phase solubility, as well as the partition coefficients, of these particular triarylphosphines in fluorous biphasic solvent systems displays an optimum at ca. 63 wt % fluorine. Only in the case of *c*-$C_6F_{11}CF_3$/*n*-pentane did we observe a steady increase of the fluorous phase affinity with the amount of fluorous character, resulting in an optimum for 67 wt % fluorine. Interestingly, there is a strong correlation between the single phase fluoro- and hydrocarbon solubility of these fluorous phosphines and their fluorous phase affinity in fluorous biphasic systems.

Especially the phase partitioning of uncoordinated fluorous ligands is a particularly relevant issue for fluorous biphasic catalyst separation, as ligand dissociation is often an essential step in the catalytic cycle. Leaching of dissociated ligand into the nonfluorous phase is, therefore, a possible catalyst deactivation pathway. With this aspect in mind, we are currently further investigating fluorous catalysts based on our 6- and 9-fluorotail-containing phosphines.

Experimental Section

General Remarks. Reactions were conducted in a dinitrogen atmosphere unless noted otherwise. Solvents were obtained and prepared as follows: benzene, toluene, *n*-pentane, *n*-hexane, and diethyl ether were distilled from Na/benzophenone; FC-72, *c*-$C_6F_{11}CF_3$, $CF_3C_6H_5$ (Acros, Alfa), C_6F_6 (Acros), C_6D_6, $CDCl_3$, and *n*-C_6D_{14} (Cambridge Isotope Laboratories, Aldrich) were degassed and stored over molecular sieves. Reagents were obtained and prepared as follows: $C_xF_{2x+1}CH{=}CH_2$ ($x = 6, 8$) (Acros), $C_xF_{2x+1}CH_2CH_2I$ ($x = 6, 8$) (Lancaster), and Mg turnings (Norsk Hydro, >99.8%) were used as received; $HSiCl_3$, $HSi(Me)Cl_2$, $HSiMe_2Cl$, and H_2PtCl_6(aq) (Acros) were stored under nitrogen and used as received. Elemental and ICP−AAS analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mühlheim an der Ruhr, Germany. ^{31}P NMR spectra were referenced relative to 85% H_3PO_4 and ^{19}F NMR spectra relative to $CFCl_3$ (both external). The ^{19}F decoupler frequency in $^{13}C\{^{19}F\}$ NMR experiments was set to either $\delta = -121$ or $\delta = -81$ to decouple from the ^{19}F nuclei of the CF_2 moieties or the CF_3 group, respectively. For the simulation of ^{1}H NMR spectra, the computer program gNMR, version 3.6, Cherwell Scientific Publishing Limited, Oxford, was used.

Caution: Although the toxicity of the fluorous phosphines developed is unknown, they are lipophilic and, therefore, expected to be able to accumulate in body tissues, analogous to behavior observed for perfluorocarbons.[28] Hence, proper precautions should be taken to prevent, for example, contact with the skin.

General Procedure for Reaction of the Grignard Reagents of 2-(Perfluoroalkyl)iodoethanes with Chlorosilanes. The freshly prepared and filtered $C_xF_{2x+1}(CH_2)_2I$ Grignard solution was treated with a stoichiometric amount (based on 90% conversion of the Grignard reaction) of the respective chlorosilane and stirred overnight. The reaction mixture, which consisted of either a liquid biphasic system or a white suspension, was quenched with water (100 mL). After phase separation, the organic phase was combined with two 20-mL diethyl ether extracts of the water phase, and the resulting mixture was dried over $MgSO_4$. Volatiles were removed using a rotary evaporator. The light-yellow oils (**B**{**2,6**}, **B**{**3,6**}, and **B**{**1,8**}) and white, waxy solids (**B**{**2,8**} and **B**{**3,8**}) contained ≤10% of the Wurtz coupling product, which was removed by Kugelrohr distillation or by fractional distillation (**B**{**1,6**}).

Methyl[bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)]silane (B{2,6}). A Grignard solution prepared from 12.5 g (26 mmol) of $C_6F_{13}(CH_2)_2I$ treated with 1.24 mL (1.38 g, 12.0 mmol) of $HSiMeCl_2$ yielded 7.68 g (10.4 mmol, 79% based on 1H,1H,2H,2H-perfluorooctyl iodide). Bp: 96 °C (0.1 Torr). ^{1}H NMR (δ, $CDCl_3$): 3.91 (oct, $^1J_{Si,H} = 187$ Hz, $^3J_{H,H} = 3.8$ Hz, 1H), 2.10 (m, 4H), 0.90 (m, 4H), 0.19 (d, $^3J_{H,H} = 3.8$ Hz, 3H). ^{19}F NMR (δ, $CDCl_3$): −82.0 (m, 3F), −117.1 (m, $J_{F,F} = 15$ Hz, 2F), −123.0 (m, 2F), −124.0 (m, 2F), −124.5 (m, 2F), −127.3 (m, 2F). ^{29}Si$\{^1$H$\}$ NMR (δ, $CDCl_3$): −6.78. $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 26.4 (t, $^2J_{C,F} = 23$ Hz), 2.33, −6.74.

Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)methylsilane (B{2,8}). A Grignard solution prepared from 26.2 g (45.6 mmol) of $C_8F_{17}(CH_2)_2I$ treated with 2.13 mL (2.36 g, 20.5 mmol) of $HSiMeCl_2$ yielded 14.9 g (15.9 mmol, 69.7% based on 1H,1H,2H,2H-perfluoroalkyl iodide). Mp: 38−40 °C. Anal. Calcd for $C_{21}H_{12}F_{34}Si$: C, 26.85; H, 1.28; F, 68.84; Si, 2.98. Found: C, 26.95; H, 1.36; F, 68.66; Si, 2.91. ^{1}H NMR (δ, $CDCl_3$): 3.91 (oct, $^1J_{Si,H} = 191$ Hz, $^3J_{H,H} = 3.6$ Hz, 1H), 2.11 (m, 4H), 0.91 (m, 4H), 0.20 (d, $^3J_{H,H} = 3.6$ Hz, 3H). ^{19}F NMR (δ, $CDCl_3$): −81.7 (m, 3F), −116.9 (m, $J_{F,F} = 12$ Hz, 2F), −122.7 (m, 6F), −123.5 (m, 2F), −124.1 (m, 2F), −127.0 (m, 2F). ^{29}Si NMR (δ, $CDCl_3$): −6.81 (d, $^1J_{Si,H} = 192$ Hz). ^{29}Si$\{^1$H$\}$ NMR (δ, $CDCl_3$): −6.77. $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 26.4 (t, $^2J_{C,F} = 24$ Hz), 2.26, −6.86. $^{13}C\{^{19}F\}$ NMR (δ, $CDCl_3$): 118.4 (m), 117.5 (q, $^1J_{C,F} = 269$ Hz), 111.7, 111.5, 111.2, 111.1, 110.6, 108.8 (q, $^2J_{C,F} = 26.3$ Hz), 26.6 (tm, $^1J_{C,H} = 130$ Hz), 2.42 (tm, $^1J_{C,H} = 119$ Hz), −7.01 (qm, $^1J_{C,H} = 121$ Hz).

Tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane (B{3,8}). A Grignard solution prepared from 24.5 g (42.6 mmol) of $C_8F_{17}(CH_2)_2I$ treated with 1.08 mL (1.44 g, 10.7 mmol) of $HSiCl_3$ yielded 14.7 g (10.7 mmol, 75% based on 1H,1H,2H,2H-perfluoroalkyl iodide). Mp: 91 °C. Anal. Calcd for $C_{30}H_{13}F_{51}Si$: C, 26.27; H, 0.95; F, 70.71; Si, 2.04. Found: C, 26.16; H, 1.10; F, 70.62; Si, 2.18. ^{1}H NMR (δ; $CDCl_3$/C_6F_6, 3:1 (v/v)): 3.9 (m, $^1J_{Si,H} = 192$ Hz, 1H), 2.13 (m, 6H), 1.05 (m, 6H). ^{19}F NMR (δ; $CDCl_3$/C_6F_6, 3:1 (v/v)): −81.7 (m, 3F), −116.9 (m, 2F), −122.7 (m, 6F), −123.6 (m, 2F), −124.2 (m, 2F), −127.0 (m, 2F). ^{29}Si$\{^1$H$\}$ NMR (δ; $CDCl_3$/C_6F_6, 3:1 (v/v)): −2.38. $^{13}C\{^{19}F\}$ NMR (δ; $CDCl_3$/C_6F_6, 3:1 (v/v)): 118.5 (m), 117.8 (q, $^1J_{C,F} = 262$ Hz), 111.8, 111.8, 111.4, 111.4, 110.9, 109.0 (q, $^2J_{C,F} = 24.4$ Hz), 26.6 (tm, $^1J_{C,H} = 130$ Hz), 1.0 (tm, $^1J_{C,H} = 124$ Hz).

General Procedure for Bromination of 2-(Perfluoroalkyl)ethylsilanes B{*n*,*x*}. The silanes **B**{***n*,*x***} were dissolved in either *n*-hexane or *n*-hexane/FC-72 mixtures, and a 2-fold excess of Br_2 was added to the reaction mixture at 0 °C. After

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the reaction mixture was stirred for 15 h at room temperature, all of the volatiles were removed in vacuo. The slightly yellow or colorless oils or waxy solids were further purified by Kugelrohr distillation, fractional distillation, or recrystallization, when necessary.

Bromo(methyl)[bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)]silane (C{2,6}). A solution of 25.4 g (34.3 mmol) of **B**{**2,6**} in 100 mL of *n*-hexane was treated with 3.51 mL (11.0 g, 68.7 mmol) of Br_2, yielding 27.6 g (34.0 mmol, 99% based on **B**{**2,6**}) of the title compund. Bp: 105 °C (0.1 Torr). ^{1}H NMR (δ, C_6D_6): 1.93 (m, 4H), 0.71 (m, 4H), 0.02 (s, 3H). ^{19}F NMR (δ, C_6D_6): −81.5 (t, $J_{F,F}$ = 9 Hz, 3F), −115.7 (m, $J_{F,F}$ = 15 Hz, 2F), −122.3 (m, 2F), −123.3 (m, 2F), −123.5 (m, 2F), −126.6 (m, 2F). ^{29}Si{^{1}H} NMR (δ, C_6D_6): 29.2. ^{13}C{^{1}H} NMR (δ, C_6D_6): 118.8 (tt, $^1J_{C,F}$ = 255 Hz, $^2J_{C,F}$ = 30.6 Hz), 118.1 (qt, $^1J_{C,F}$ = 289 Hz, $^2J_{C,F}$ = 33.0 Hz), 112.3 (tquin, $^1J_{C,F}$ = 268 Hz, $^2J_{C,F}$ = 32.0 Hz), 112.1 (tquin, $^1J_{C,F}$ = 271.3 Hz, $^2J_{C,F}$ = 31.8 Hz), 111.3 (tquin, $^1J_{C,F}$ = 272 Hz, $^2J_{C,F}$ = 31.7 Hz), 109.4 (tqt, $^1J_{C,F}$ = 260 Hz, $^2J_{C,F}$ = 30.5 Hz), 26.0 (t, $^2J_{C,F}$ = 23.8 Hz), 7.73, −0.38.

Bromo[bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)]methylsilane C{2,8}. A solution of 24.6 g (26.2 mmol) of **B**{**2,8**} in 400 mL of *n*-hexane was treated with 2.7 mL (8.4 g, 52 mmol) of Br_2, yielding 21.3 g (20.9 mmol, 80% based on **B**{**2,8**}) of the title compound after recrystallization in benzene. Mp: 55 °C. Anal. Calcd for $C_{21}H_{11}BrF_{34}Si$: C, 24.77; H, 1.08; Br, 7.85; F, 63.50; Si, 2.75. Found: C, 24.87; H, 1.15; Br, 7.67; F, 63.62; Si, 2.69. ^{1}H NMR (δ, C_6D_6): 2.00 (m, 4H), 0.84 (m, 4H), 0.12 (s, $^2J_{Si,H}$ = 6.6 Hz, 3H). ^{19}F NMR (δ, C_6D_6): −81.0 (m, 3F), −115.2 (m, 2F), −121.7 (m, 6F), −122.5 (m, 2F), −122.9 (m, 2F), −126.0 (m, 2F). ^{29}Si{^{1}H} NMR (δ, C_6D_6): 29.1. ^{13}C{^{19}F} NMR (δ, C_6D_6): 118.7 (m), 117.9 (q, $^1J_{C,F}$ = 272 Hz), 112.0, 111.7, 111.6, 111.1, 109.8 (m), 25.9 (tt, $^1J_{C,H}$ = 131 Hz, $^2J_{C,H}$ = 5.5 Hz), 7.61 (tm, $^1J_{C,H}$ = 122 Hz), −0.31 (qm, $^1J_{C,H}$ = 123 Hz).

Bromo[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)]silane (C{3,8}). A biphase liquid system of 12.6 g (8.72 mmol) of **B**{**3,8**} in 40 mL of FC-72 and 30 mL of *n*-hexane was treated with 1.0 mL (3.12 g, 19.5 mmol) of Br_2, yielding 11.6 g (8.00 mmol, 91.7% based on **B**{**3,8**}) of pure **C**{**3,8**}. Mp: 93 °C. ^{1}H NMR (δ; C_6D_6/C_6F_6, 3:1 (v/v)): 2.21 (m, 6H), 1.13 (m, 6H). ^{19}F NMR (δ; C_6D_6/C_6F_6, 3:1 (v/v)): −81.6 (m, 3F), −116.0 (m, 2F), −121.9 (m, 6F), −122.8 (m), −123.1 (m, 2F), −126.3 (m, 2F). ^{29}Si{^{1}H} NMR (δ; C_6D_6/C_6F_6, 3:1 (v/v)): 30.1.

1-Bromo-4-[{2-(perfluoroalkyl)ethyl}dimethylsilyl]-benzenes and 1-Bromo-4-(trimethylsilyl)benzene. General Procedure. *p*-LiC_6H_4Br was obtained from *p*-bromoiodobenzene and 1 equiv of ^{n}BuLi (1.5 M solution in *n*-hexane) diluted in *n*-pentane at 0 °C. After 1 h, the suspension was centrifuged, and the liquid was decanted off from the white precipitate. The corresponding chlorosilane dissolved in 10 mL of THF was added at −78 °C to a suspension of *p*-LiC_6H_4Br in *n*-pentane. The reaction mixture was allowed to warm to room temperature and was stirred overnight. After the reaction was quenched with saturated NH_4Cl(aq), the water phase was extracted with two 20-mL portions of *n*-pentane. The combined organic phases were dried over $MgSO_4$. Fractional distillation afforded the pure products. Compounds 1,4-$(RMe_2Si)_2C_6H_4$ (R = Me, $(CH_2)_2C_6F_{13}$, $(CH_2)_2C_8F_{17}$) were obtained as colorless solids.

1-Bromo-4-[dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]benzene (E{1,6}). Compound **C**{**1,6**} (3.58 g, 7.57 mmol) and *p*-LiC_6H_4Br, obtained from 2.4 g (8.48 mmol) of *p*-bromoiodobenzene and 5.6 mL (8.4 mmol) of ^{n}BuLi solution in *n*-pentane (40 mL), yielded 3.53 g (6.29 mmol, 83% based on **C**{**1,6**}) of the title compound. Bp: 104 °C (0.1 Torr). ^{1}H NMR (δ; C_6D_6/C_6F_6, 1:1 (v/v)): 7.25 (m, 2H), 7.12 (m, 2H), 2.02 (m, 2H), 0.94 (m, 2H), 0.22 (s, 6H). ^{19}F NMR (δ, C_6D_6): −81.4 (m, 3F), −116.4 (m, 2F), −122.5 (m, 2F), −123.5 (m, 2F), −123.8 (m, 2F), −126.7 (m, 2F). ^{29}Si{^{1}H} NMR (δ; C_6D_6/C_6F_6, 1:1 (v/v)): −1.51. ^{13}C{^{1}H} NMR (δ, C_6D_6): 136.3, 135.6, 131.9, 125.0, 119.3 (tt, $^1J_{C,F}$ = 255 Hz, $^2J_{C,F}$ = 29.8 Hz), 118.2 (qt, $^1J_{C,F}$ = 287 Hz, $^2J_{C,F}$ = 31.7 Hz), 112.3 (tquin, $^1J_{C,F}$ = 268 Hz), 112.2 (tquin, $^1J_{C,F}$ = 270 Hz, $^2J_{C,F}$ = 32.5 Hz), 111.3 (tquin, $^1J_{C,F}$ = 274 Hz, $^2J_{C,F}$ = 31.6 Hz), 109.5 (tqt, $^1J_{C,F}$ = 270 Hz, $^2J_{C,F}$ = 31.6 Hz), 26.5 (t, $^2J_{C,F}$ = 23.7 Hz), 5.56 (s, $^1J_{C,Si}$ = 50.5 Hz), −3.65 (s, $^1J_{C,Si}$ = 52.8 Hz).

Side Product 1,4-[$C_6F_{13}(CH_2)_2SiMe_2]_2C_6H_4$. ^{1}H NMR ($\delta$, $CDCl_3$): 7.34 (s, 4H), 2.02 (m, 4H), 0.74 (m, 4H), 0.11 (s, 12H, $^2J_{Si,H}$ = 6.6 Hz). ^{13}C{^{1}H} NMR (δ, C_6D_6): 139.0, 133.6, 26.6 (t, $^2J_{C,F}$ = 24.2 Hz), 5.66 (t, $^3J_{C,F}$ = 2.1 Hz), −3.34 (s, $^1J_{C,Si}$ = 60.5 Hz).

1-Bromo-4-[3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl(dimethyl)silyl]benzene (E{1,8}). Compound **C**{**1,8**} (21.9 g, 40.5 mmol) and *p*-LiC_6H_4Br, obtained from 12.6 g (44.5 mmol) of *p*-bromoiodobenzene and 27 mL (40.5 mmol) of ^{n}BuLi solution in *n*-pentane (80 mL), yielded 23.3 g (35.2 mmol, 87% based on **C**{**1,8**}) of the title compound. Bp: 145−150 °C (0.1 Torr). Mp: 38 °C. ^{1}H NMR (δ, C_6D_6): 7.31 (m, 2H), 6.89 (m, 2H), 1.84 (m, 2H), 0.75 (m, 2H), −0.06 (s, 6H, $^2J_{Si,H}$ = 6.4 Hz). ^{13}C{^{1}H} NMR (δ, C_6D_6): 136.3, 135.6, 131.9, 125.0, 119.3 (tt, $^1J_{C,F}$ = 254 Hz, $^2J_{C,F}$ = 31.1 Hz), 118.0 (qt, $^1J_{C,F}$ = 288 Hz, $^2J_{C,F}$ = 33.0 Hz), 112.7, 112.7, 111.9, 111.9 (tm), 111.2 (tm), 109.1 (tm), 26.5 (t, $^2J_{C,F}$ = 23.8 Hz), 5.56 (s, $^1J_{C,Si}$ = 50.7 Hz), −3.65 (s, $^1J_{C,Si}$ = 53.1 Hz).

Side Product 1,4-[$C_8F_{17}(CH_2)_2SiMe_2]_2C_6H_4$. ^{1}H NMR ($\delta$, $CDCl_3$): 7.48 (s, 4H), 1.99 (m, 4H), 0.96 (m, 4H), 0.31 (s, 12H).

Tris[4-{dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl}phenyl]phosphine (D{1,6}) through Route a. Compound **E**{**1,6**} (6.1 g, 11 mmol) in 50 mL of *n*-hexane was treated with 14.5 mL (21.7 mmol) of ^{t}BuLi (1.50 M solution in *n*-hexane) at −78 °C. The reaction mixture was allowed to reach room temperature and then stirred for 15 h. The white precipitate formed was washed with *n*-pentane (2 × 20 mL) and suspended in diethyl ether (50 mL). Solids were removed by centrifuge, and the clear solution was evaporated to dryness, affording 4.89 g of the lithiated aryl compound, which contained 1 equiv of diethyl ether (^{1}H NMR). This material (4.19 g) in a mixture of *n*-hexane (30 mL) and THF (5 mL) was treated with PCl_3 (0.25 mL, 2.84 mmol) in *n*-hexane (5 mL) at −78 °C. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred for another 15 h. Volatiles were removed in vacuo after filtration, and the white residue was extracted with *n*-pentane (3 × 20 mL). The volume of the combined *n*-pentane phases was reduced to 10 mL, and the extract was stored at −10 °C. The mother liquor was decanted, and the white precipitate was dried in vacuo. Yield: 2.85 g (1.93 mmol, 62% based on **E**{**1,6**}). Mp: 89 °C. Anal. Calcd for $C_{48}H_{42}F_{39}Si_3P$: C, 39.1; H, 2.85; F, 50.3; Si, 5.71; P, 2.10. Found: C, 39.3; H, 2.87; F, 50.1; Si, 5.80; P, 2.08. ^{1}H NMR (δ; C_6D_6/C_6F_6, 1:1 (v/v)): 7.33 (m, 2H), 7.25 (m, 2H), 2.04 (m, 2H), 0.97 (m, 2H), 0.26 (s, 6H). ^{31}P{^{1}H} NMR (δ; C_6D_6/C_6F_6, 1:1 (v/v)): −4.66. ^{29}Si{^{1}H} NMR (δ; C_6D_6/C_6F_6, 1:1 (v/v)): −1.69. ^{19}F NMR (δ, C_6D_6): −81.4 (tt, $J_{F,F}$ = 9.7 Hz, $J_{F,F}$ = 2.5 Hz, 3F), −115.8 (m, 2F), −122.2 (m, 2F), −123.2 (m, 2F), −123.3 (m, 2F), −126.5 (m, 2F). ^{13}C{^{1}H} NMR (δ, C_6D_6): 139.4 (d, $^1J_{P,C}$ = 12.7 Hz), 138.7 ($^1J_{Si,C}$ = 65 Hz), 134.3 (d, $^3J_{P,C}$ = 6.7 Hz), 134.1 (d, $^2J_{P,C}$ = 18.9 Hz), 119.3 (tt, $^1J_{C,F}$ = 254 Hz, $^2J_{C,F}$ = 30.5 Hz), 118.1 (qt, $^1J_{C,F}$ = 289 Hz, $^2J_{C,F}$ = 33.3 Hz), 112.3 (tquin, $^1J_{C,F}$ = 268 Hz, $^2J_{C,F}$ = 32.0 Hz), 112.1 (tquin, $^1J_{C,F}$ = 271 Hz, $^2J_{C,F}$ = 31.8 Hz), 111.3 (tquin, $^1J_{C,F}$ = 272 Hz, $^2J_{C,F}$ = 31.7 Hz), 109.4 (tqt, $^1J_{C,F}$ = 260 Hz, $^2J_{C,F}$ = 30.5 Hz), 26.6 (t, $^2J_{C,F}$ = 23.5 Hz), 5.62 (s, $^1J_{C,Si}$ = 50.9 Hz), −3.51 (s, $^1J_{C,Si}$ = 53.1 Hz). ^{13}C{^{19}F} NMR (δ, C_6D_6): 139.4 (dt, $^1J_{P,C}$ = 12.8 Hz), 138.6, 134.2 (dm), 119.3 (s), 118.1 (q, $^1J_{C,F}$ = 269 Hz), 112.3, 112.1, 111.3, 109.5 (q, $^2J_{C,F}$ = 25.1 Hz), 26.6 (tm, $^1J_{C,H}$ = 125 Hz), 5.57 (t, $^1J_{C,H}$ = 121 Hz), 4.34 (q, $^1J_{C,H}$ = 121 Hz).

Tris[4-{(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl}phenyl]phosphine (D{1,8}) through Route a. A solution of 4.36 g (6.59 mmol) of **E**{**1,8**} in 30 mL of *n*-hexane was treated with 4.39 mL (6.58 mmol) of ^{n}BuLi solution at 0 °C and stirred for 15 h at room temperature. The voluminous white precipitate that separated was washed with *n*-hexane (20 mL) and dried in vacuo to afford 2.74 g of lithiated product. Alternatively, 9.28 g (14.0 mmol) of **E**{**1,8**} in 50 mL of *n*-hexane and 18.7 mL (28.1 mmol) of ^{t}BuLi solution at −78 °C afforded, through a similar workup, 7.07 g of a 1:1 mixture of the lithiated aryl compound and LiBr. Lithiated **E**{**1,8**} (2.74 g, 4.65 mmol) in a mixture

of *n*-hexane (30 mL) and THF (5 mL) was treated with 0.135 mL (1.55 mmol) of PCl_3 in *n*-hexane (5 mL) at −78 °C. A workup similar to that for **D**{**1,6**} yielded 1.59 g of **D**{**1,8**} (0.89 mmol, 41% based on **E**{**1,8**}). Alternatively, 7.07 g of the 1:1 mixture of lithiated **E**{**1,8**} and LiBr was suspended in *n*-pentane (100 mL) and treated with $P(OMe)_3$ (0.41 mL, 3.48 mmol) at 0 °C, yielding 4.00 g of **D**{**1,8**} (2.25 mmol, 48% based on E{**1,8**}), through a workup procedure similar to that for **D**{**1,6**}. Mp: 101 °C. Anal. Calcd for $C_{54}H_{42}F_{51}Si_3P$: C, 36.52; H, 2.34; F, 54.6; Si, 4.74; P, 1.75. Found: C, 36.6; H, 2.41; F, 54.4; Si, 4.85; P, 1.86. ^{1}H NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 7.34 (m, 2H), 7.25 (m, 2H), 2.04 (m, 2H), 0.98 (m, 2H), 0.27 (s, 6H). ^{31}P{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −4.67. ^{29}Si{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −1.69. ^{13}C{^{19}F} (*δ*, C_6D_6): 139.4 (dt, $^1J_{P,C}$ = 12.7 Hz, $^2J_{C,H}$ = 6.1 Hz), 138.6 (m), 134.3 (dm), 134.1 (dm), 119.3 (m), 118.1 (q, $^1J_{C,F}$ = 268 Hz), 112.3, 112.2, 111.8, 111.7, 111.1, 109.3 (qm, $^2J_{C,F}$ = 26 Hz), 26.5 (tt, $^1J_{C,H}$ = 129 Hz, $^2J_{F,F}$ = 5.5 Hz), 5.58 (t, $^1J_{C,H}$ = 121 Hz), −3.51 (q, $^1J_{C,H}$ = 119 Hz). ^{19}F NMR (*δ*, C_6D_6): −81.4 (m, 3F), −116.7 (m, 2F), −122.2 (m, 6F), −123.0 (m, 2F), −123.7 (m, 2F), −126.8 (m, 2F).

Tris[4-{(2-((perfluoroalkyl)ethyl)silyl}phenyl]phosphines (D{*n,x*}) through Route b. General Procedure. $P(C_6H_4$-*p*-$Br)_3$ was dissolved in diethyl ether and treated with 6 equiv of ^{t}BuLi (1.5 M in *n*-hexane) at −78 °C. After 10 min, when a voluminous white precipitate had formed, a solution of the fluorous bromosilane **C**{*n,x*} in diethyl ether was added. The reaction mixture was allowed to reach room temperature and was stirred for another 15 h. In case the phosphines did not precipitate quantitatively, the reaction mixture was filtered, and the product was dried in vacuo. All volatiles of the filtrate were removed in vacuo, and the residue was extracted in 50 mL of FC-72. The remainder of the product was isolated from the filtrate by removal of the volatiles in vacuo. Minor amounts of impurities were removed by washing with *n*-pentane.

Tris[4-{dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl}phenyl]phosphine (D{1,6}). Compound **C**{**1,6**} (6.09 g, 13.8 mmol) added to a suspension of $P(C_6H_4$-*p*-$Li)_3$, obtained from 2.30 g (4.61 mmol) of $P(C_6H_4$-*p*-$Br)_3$ in 50 mL of hexane/diethyl ether (3:1, v/v) and 18.4 mL (27.7 mmol) of ^{t}BuLi solution, yielded 5.23 g (3.53 mmol, 77% based on **C**{**1,6**}) of the title compound, after quenching of the reaction with degassed water (20 mL), phase separation, and extraction with diethyl ether (30 mL).

Tris[4-{methyl(bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl))silyl}phenyl]phosphine (D{2,6}). Compound **C**{**2,6**} (9.43 g, 11.6 mmol) in 150 mL of diethyl ether added to a suspension of $P(C_6H_4$-*p*-$Li)_3$, obtained from 2.09 g (4.19 mmol) of $P(C_6H_4$-*p*-$Br)_3$ in 100 mL of diethyl ether and 16.6 mL (24.9 mmol) of ^{t}BuLi solution, yielded 9.37 g (3.79 mmol, 98% based on **C**{**2,6**}) of the title compound. Mp: 67 °C. Anal. Calcd for $C_{69}H_{45}F_{78}Si_3P$: C, 33.50; H, 1.82; F, 59.97; Si, 3.40; P, 1.25. Found: C, 33.64; H, 1.95; F, 60.11; Si, 3.32; P, 1.22. ^{1}H NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 7.32 (m, 6H), 7.28 (m, 6H), 2.02 (m, 12H), 1.01 (m, 12H), 0.24 (s, 9H). ^{31}P{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −4.62. ^{29}Si{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 0.24. ^{19}F NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −81.5 (m, 3F), −116.0 (m, 2F), −122.0 (m, 2F), −123.0 (m, 2F), −123.3 (m, 2F), −126.4 (m, 2F). ^{13}C{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 139.0 (m), 138.3, 134.4 (dm), 119.4 (s), 118.5 (q, $^1J_{C,F}$ = 271 Hz), 112.6, 112.5, 111.7, 109.9, 26.6 (tm, $^1J_{C,H}$ = 130 Hz), 4.06 (t, $^1J_{C,H}$ = 120 Hz), −6.45 (q, $^1J_{C,H}$ = 120 Hz).

Tris[4-{tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silyl}phenyl]phosphine (D{3,6}). Compound **C**{**3,6**} (16.4 g, 14.3 mmol) in 100 mL of diethyl ether added to a suspension of $P(C_6H_4$-*p*-$Li)_3$, obtained from 2.38 g (4.77 mmol) of $P(C_6H_4$-*p*-$Br)_3$ in 100 mL of diethyl ether and 19.1 mL (28.6 mmol) of ^{t}BuLi solution, yielded 14.2 g (4.09 mmol, 86% based **C**{**3,6**}) of the title compound. Mp: 50−55 °C. Anal. Calcd for $C_{90}H_{48}F_{117}Si_3P$: C, 31.2; H, 1.40; F, 64.1; Si, 2.43; P, 0.89. Found: C, 33.9; H, 1.68; F, 60.7; Si, 2.66; P, 0.96. ^{1}H NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 7.35 (m, 4H), 2.05 (m, 6H), 1.08 (m, 6H). ^{31}P{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −4.49. ^{29}Si{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 1.25. ^{19}F NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −81.5 (m, 3F), −115.9 (m, 2F), −121.9 (m, 2F), −122.9 (m, 2F), −123.2 (m, 2F), −126.3 (m, 2F).

Tris[4-{bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)methylsilyl}phenyl]phosphine (D{2,8}). Compound **C**{**2,8**} (23.2 g, 22.8 mmol) in 130 mL of diethyl ether added to a suspension of $P(C_6H_4$-*p*-$Li)_3$, obtained from 3.42 g (6.85 mmol) of $P(C_6H_4$-*p*-$Br)_3$ in 200 mL of diethyl ether and 27.4 mL (41.1 mmol) of ^{t}BuLi solution, yielded 21.0 g (6.84 mmol, 90% based on **C**{**2,8**}) of the title compound. Mp: 72 °C. Anal. Calcd for $C_{81}H_{45}F_{102}Si_3P$: C, 31.65; H, 1.46; F, 63.10; Si, 2.73; P, 1.00. Found: C, 31.71; H, 1.41; F, 62.91; Si, 2.72; P, 1.08. ^{1}H NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 7.30 (m, 4H), 2.03 (m, 4H), 1.02 (m, 4H), 0.25 (s, 3H). ^{31}P{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −4.70. ^{29}Si{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 0.23. ^{13}C{^{19}F} NMR (*δ*; C_6D_{14}/FC-72, 1:1 (v/v)): 140.4 (dt, $^1J_{P,C}$ = 14.0 Hz, $^2J_{C,H}$ = 6.7 Hz), 136.1 (m), 134.3 (dm), 119.0 (m), 118.4 (q, $^1J_{C,F}$ = 262 Hz), 112.4, 112.3, 112.0, 111.4, 109.8 (qm, $^2J_{C,F}$ = 26 Hz), 26.5 (tm, $^1J_{C,H}$ = 131 Hz), 3.98 (t, $^1J_{C,H}$ = 123 Hz), −6.98 (q, $^1J_{C,H}$ = 120 Hz). ^{19}F NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −82.4 (m, 3F), −117.0 (m, 2F), −122.8 (m, 6F), −123.7 (m, 2F), −124.1 (m, 2F), −127.2 (m, 2F).

Tris[4-{tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl}phenyl]phosphine (D{3,8}). Compound **C**{**3,8**} (17.2 g, 11.9 mmol) in 200 mL of diethyl ether added to a suspension of $P(C_6H_4$-*p*-$Li)_3$, obtained from 1.78 g (3.57 mmol) of $P(C_6H_4$-*p*-$Br)_3$ in 200 mL of diethyl ether and 14.2 mL (21.4 mmol) of ^{t}BuLi solution, yielded 15.3 g (3.50 mmol, 88% based on **C**{**3,8**}) of the title compound. Mp: 124 °C. Anal. Calcd for $C_{108}H_{48}F_{153}Si_3P$: C, 29.67; H, 1.10; F, 66.56; Si, 1.92; P, 0.71. Found: C, 29.66; H, 1.15; F, 66.38; Si, 1.96; P, 0.74. ^{1}H NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 7.35 (m, 4H), 2.07 (m, 6H), 1.09 (m, 6H). ^{31}P{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −4.49. ^{29}Si{^{1}H} NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): 1.24. ^{19}F NMR (*δ*; C_6D_6/C_6F_6, 1:1 (v/v)): −80.9 (m, 3F), −115.4 (m, 2F), −121.4 (m, 6F), −122.3 (m, 2F), −122.6 (m, 2F), −125.8 (m, 2F).

Solubility Studies. Saturated solutions in the appropriate solvent were prepared by stirring a suspension of the fluorous phosphine for 2 h at 25 °C. A sample (3.000 ± 0.002 mL) was taken after allowing the solution to settle. The total weight of the saturated solution was determined. All solvent was removed in vacuo (0.1 mbar, 15 h), after which the weight was constant within ±0.001 g, and the weight of the residue was determined.

Determination of Partition Coefficients. The partition coefficients were determinded by dissolving a known amount of phosphine (typically between 11 and 60 *μ*mol) in a fluorous biphasic system consisting of *c*-$C_6F_{11}CF_3$ (2.000 ± 0.002 mL) and either *n*-pentane, *n*-octane, or toluene (2.000 ± 0.002 mL). The resulting mixture was stirred at 25 °C until all of the solid had dissolved, and the mixture had equilibrated in a water/ice bath (1 h). An aliquot (0.500 ± 0.002 mL) was removed from each layer by syringe. Analysis by ICP−AAS on phosphorus gave the amount of phosphine present, with an accuracy of ±0.3 ppm. A conservative estimate of the experimental error in the partition coefficient is ±1 in the last digit.

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Supporting Information Available: Improved synthetic procedures for known compounds **C**{**1,6**}, **C**{**1,8**}, Grignards **A**{*x*} (*x* = 6, 8), **C**{**3,6**}, and tris(*p*-bromophenyl)phosphine; ^{1}H NMR spectra of compounds **B**{**2,6**}, **C**{**2,6**}, **C**{**3,8**}, **E**{**1,6**}, 1,4-$[C_6F_{13}(CH_2)_2SiMe_2]_2C_6H_4$, **E**{**1,8**}, and 1,4-$[C_8F_{17}(CH_2)_2$-$SiMe_2]_2C_6H_4$; ^{13}C NMR spectra of compounds **B**{**2,6**}, **C**{**2,6**}, **E**{**1,6**}, 1,4-$[C_6F_{13}(CH_2)_2SiMe_2]_2C_6H_4$, **E**{**1,8**}, and 1,4-$[C_8F_{17}(CH_2)_2$-$SiMe_2]_2C_6H_4$; and ^{19}F and ^{29}Si NMR spectra of compounds **B**-{**2,6**}, **C**{**2,6**}, **C**{**3,8**}, and **E**{**1,6**}. This material is available free of charge via the Internet at http://pubs.acs.org.

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