

Highly Fluorous Derivatives of 1,2-Bis(diphenylphosphino)ethane

Elwin de Wolf,[†] Bodo Richter,[†]
Berth-Jan Deelman,^{*,‡} and Gerard van Koten[†]

Debye Institute, Department of Metal-Mediated
Synthesis, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands, and Elf
Atochem Vlissingen B.V., P.O. Box 70,
4380 AB Vlissingen, The Netherlands

b.j.deelman@chem.uu.nl

Received March 6, 2000

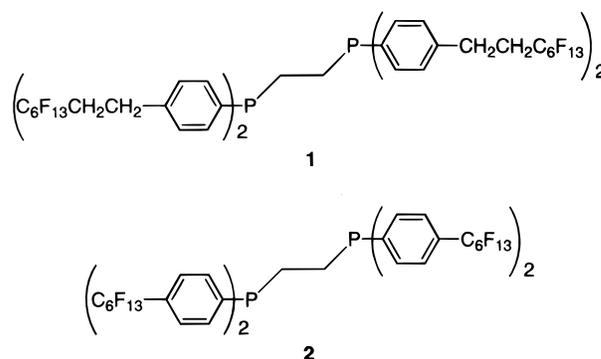
Introduction

Since the first demonstration of catalyst recovery using the technique of fluororous biphasic separation,¹ several classes of ligands have been functionalized with perfluoroalkyl chains to increase solubility of these ligands and derived catalysts in fluororous solvents.² Published work concerning phosphorus ligands has been mainly focused on fluororous versions of monodentate tertiary phosphines which contain hydrocarbon spacers to insulate the phosphorus atom from the electron-withdrawing effect of the perfluoroalkyl tails.³ Triarylphosphines with perfluoroalkyl tails directly connected to the aryl ring⁴ and through a $-\text{CH}_2\text{CH}_2-$ spacer⁵ as well as perfluoroalkylated phosphinites,⁶ -phosphonites,⁶ and -phosphites⁷ have been prepared. However, performance of these ligands in catalysis is often lower compared with conventional nonfluororous ligands.

To counteract this drop in activity upon fluorotail functionalization, we introduced the $-\text{CH}_2\text{CH}_2\text{SiR}_2-$ spacer ($\text{R} = \text{Me}$ or $-\text{CH}_2\text{CH}_2\text{C}_m\text{F}_{2m+1}$) to prepare fluororous 2,6-bis[(dimethylamino)methyl]arylnickel- and platinum-,⁸ fluororous triarylphosphine rhodium,⁹ and chiral arenethiolate zinc complexes¹⁰ containing perfluoroalkyl tails. All of these catalysts displayed similar activity as

their nonfluororous counterparts. The weakly electron-donating character of the silyl substituent, which compensates for the electron-withdrawing effect of the perfluoroalkyl tail, is most probably responsible for this retention of catalytic activity. An additional advantage of the $-\text{CH}_2\text{CH}_2\text{SiR}_2-$ spacer is the possibility to connect multiple (up to three) perfluoroalkyl tails per aryl ring via the Si-center through straightforward synthetic methodologies.^{9,11} This latter characteristic allows the synthesis of ligands and derived transition metal complexes with high fluorophase affinity. Application of these ligands in fluororous biphasic metal-catalyzed organic synthesis is expected to result in improved catalyst recycling.

The fact that monophosphines are known to dissociate easily from the metal center under catalytic conditions may result in leaching of the free fluororous ligand into the organic phase.^{9d} To counteract this obvious disadvantage of the use of monophosphines in catalysis, chelating diphosphines have found widespread application in transition metal-based homogeneous catalysis.¹² Two fluororous examples of 1,2-bis(diphenylphosphino)ethane (dppe) containing four perfluoroalkyl tails (**1** and **2**) were recently reported.^{4a,5} However, studies which employ **1** in fluororous biphasic catalysis have not been reported. Diphosphine **2** was applied in fluororous biphasic hydrogenation of styrene, using $[\text{Rh}(\mu\text{-Cl})_2(\mathbf{2})_2]$ as catalyst.¹³ The activity of this system, however, was modest in comparison with the more commonly used $[\text{Rh}(\text{diene})(\text{diphosphine})]^+$ systems.^{12,14} Since diphosphine catalysts which combine high fluororous phase retention with high catalytic activity have not been reported yet, we have now employed silyl spacers to prepare highly fluororous derivatives of dppe, stimulated by the positive results obtained for fluororous triarylphosphines. The synthetic results along with some quantitative solubility studies of the diphosphines are presented below.



Results and Discussion

Starting compound 1,2-bis[bis(4-bromophenyl)phosphino]ethane (**3**) was easily obtained by addition of 1,2-bis(dichlorophosphino)ethane to a suspension of $p\text{-BrC}_6\text{H}_4\text{-}$

(9) (a) Richter, B.; De Wolf, A. C. A.; Van Koten, G.; Deelman, B. Y. PCT Int. Appl. WO 0018444, 2000, to Elf Atochem. (b) Richter, B.; Van Koten, G.; Deelman, B.-J. *J. Mol. Catal. (A), Chem.* **1999**, *145*, 317–321. (c) Richter, B.; De Wolf, E.; Van Koten, G.; Deelman, B.-J. *J. Org. Chem.* **2000**, *65*, 3385–3893. (d) Richter, B.; Spek, A. L., Van Koten, G.; Deelman, B.-J. *J. Am. Chem. Soc.*, **2000**, *122*, 3945–3951.

(10) Kleijn, H.; Rijnberg, E.; Jastrzebski, J. T. B. H.; Van Koten, G. *Org. Lett.* **1999**, *1*, 853–855.

[†] Debye Institute.

[‡] Elf Atochem, currently based at the Debye Institute. Fax: +31 30 252 3615.

(1) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72–75.

(2) (a) De Wolf, E.; Van Koten, G.; Deelman, B.-J. *Chem. Soc. Rev.* **1999**, *28*, 37–41. (b) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641–650. (c) Curran, D. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1174–1196. (d) Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2057–2059. (e) Hope, E. G.; Stuart, A. M. *J. Fluorine Chem.* **1999**, *100*, 75–83.

(3) (a) Horváth, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rábai, J.; Mozelski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133–3143. (b) Sinou, D.; Pozzi, G.; Hope, E. G.; Stuart, A. M. *Tetrahedron Lett.* **1999**, *40*, 849–852. (c) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A. *J. Org. Chem.* **1998**, *63*, 6302–6308. (d) Klose, A.; Gladysz, J. A. *Tetrahedron: Asymmetry* **1999**, *10*, 2665–2674. (e) Juliette, J. J. J.; Rutherford, D.; Horváth, I. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 2696–2704.

(4) (a) Bhattacharyya, P.; Gudmunsen, D.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Stuart, A. M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3609–3612. (b) Betzemeier, B.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2623–2624.

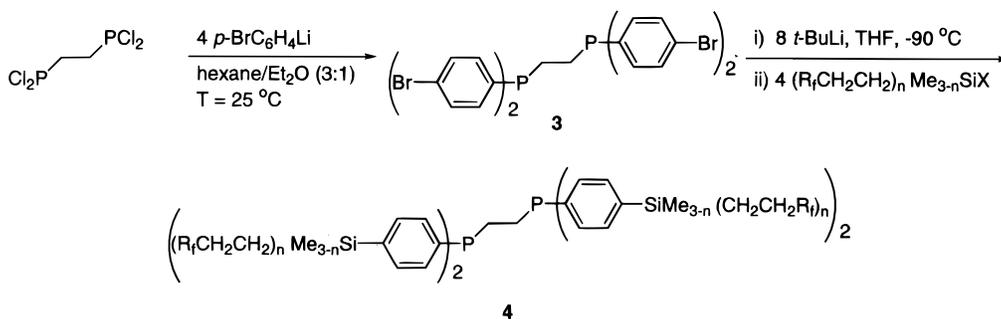
(5) Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628–1630.

(6) Haar, C. M.; Huang, J.; Nolan, S. P.; Petersen, J. P. *Organometallics* **1998**, *17*, 5018–5024.

(7) Mathivet, T.; Monflier, E.; Castanet, Y.; Morteaux, A.; Couturier, J.-L. *Tetrahedron Lett.* **1998**, *39*, 9411–9414.

(8) Kleijn, H.; Jastrzebski, J. T. B. H.; Gossage, R. A.; Kooijman, H.; Spek, A. L.; Van Koten, G. *Tetrahedron* **1998**, *54*, 1145–1152.

Scheme 1



- 4a:** $\text{R}_f = \text{C}_6\text{F}_{13}$, $n = 1$, $\text{X} = \text{Cl}$
4b: $\text{R}_f = \text{C}_6\text{F}_{13}$, $n = 2$, $\text{X} = \text{Br}$
4c: $\text{R}_f = \text{C}_6\text{F}_{13}$, $n = 3$, $\text{X} = \text{Br}$
4d: $\text{R}_f = \text{C}_8\text{F}_{17}$, $n = 1$, $\text{X} = \text{Cl}$
4e: $n = 0$, $\text{X} = \text{Cl}$

Li in a 3:1 (v/v) mixture of hexane and ether (Scheme 1). The fluorinated dppe derivatives **4a–d** were formed after lithiation of **3** in THF at $-90\text{ }^\circ\text{C}$ followed by coupling with silyl halides $(\text{R}_f\text{CH}_2\text{CH}_2)_n\text{SiMe}_{3-n}\text{X}$ ($\text{R}_f = \text{C}_6\text{F}_{13}$ or C_8F_{17} ; $\text{X} = \text{Cl}$ or Br).⁹ The products were isolated as air-stable¹⁵ white solids (**4a** and **4d**) or colorless to yellow oils (**4b** and **4c**) in high yields. Using a similar synthetic route, nonfluorous 1,2-bis[bis{4-(trimethylsilyl)phenyl}-phosphino]ethane (**4e**) was synthesized for comparison.

The fluorosilyl bromides $(\text{R}_f\text{CH}_2\text{CH}_2)_n\text{SiMe}_{3-n}\text{Br}$ ($n = 2, 3$) often contain some Wurtz-coupling product, $(\text{R}_f\text{CH}_2\text{CH}_2)_2$.^{9c} Since this side product was difficult to remove, the crude fluorosilyl bromides were used without further purification. It appeared that once the fluorosilyl bromides had been converted to the diphosphines **4b** or **4c**, the Wurtz-coupling product was easily removed by Kugelrohr distillation (**4b**) or washing with pentane (**4c**). Since $\text{R}_f\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ ($\text{R}_f = \text{C}_6\text{F}_{13}$ or C_8F_{17}) was obtained by hydrosilylation, this extra purification procedure was not necessary in the synthesis of **4a** and **4d**.

The phosphines **3** and **4a–e** were identified by both ^1H and ^{31}P NMR spectroscopy and elemental analyses. Compounds **4a** and **4d** were further characterized by their ^{19}F NMR data and **3**, **4a**, and **4e** by ^{13}C NMR spectroscopy. All spectral data corresponded to the proposed structures and no partly substituted products, bearing less than four $\text{SiMe}_{3-n}(\text{CH}_2\text{CH}_2\text{R}_f)_n$ groups, were observed. The $\text{PCH}_2\text{CH}_2\text{P}$ signal, which usually appears as a pseudo or virtual triplet in the ^1H NMR spectrum,^{4a,16} was observed as a shoulder on the $-\text{CH}_2\text{CF}_2-$ signal for **4a–d**.

The methylene carbons of the $\text{PCH}_2\text{CH}_2\text{P}$ unit as well

as the *ipso*-, *o*-, and *m*-phenyl carbons (relative to phosphorus) of phosphines **3**, **4a**, and **4e** are observed as the X part of an ABX spin system in the ^{13}C NMR spectrum.¹⁷ These observations are in close agreement with those for dppe itself.¹⁸

Comparison of the ^{31}P chemical shifts of dppe ($\delta = -11.1$) and **4a–e** in $\text{C}_6\text{D}_6/\text{C}_6\text{F}_6$ (1:1 by volume) shows a small high field shift for **4a–e** ($\delta = -11.3$ to -11.4). With some caution, it can be concluded that this is mainly caused by the *p*-silyl substitution and that the silicon spacer is indeed a good insulator for the electron-withdrawing effect of the perfluorotail.⁹

Attaching *p*- SiMe_3 groups to the aryl rings of dppe, as in **4e**, results in a large increase of the melting point (Table 1). However, when four $\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ or $\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$ tails are connected (**4a** and **4d**), the diphosphines melt at lower temperature than **4e**. Compound **4d** melts at higher temperature than **4a**, possibly due to the higher molecular weight. Similar trends in melting points were observed for related fluorosilyl triphenylphosphine derivatives.⁹ The dppe derivatives containing 8 or 12 fluorotails (**4b** and **4c**) did not solidify at room temperature.

Solubility data for the new perfluoroalkylated dppe derivatives were obtained in THF, toluene, and PFMCH (Table 1). A large difference in solubility between **4a** and **4d** was observed; the derivative with the shorter tail (**4a**) is soluble in both polar (THF, CH_2Cl_2) and aromatic organic solvents (toluene and benzene) whereas solubility in PFMCH is low. The phosphine containing the longer fluorotail (**4d**) is poorly soluble in both aromatic solvents and PFMCH. Interestingly, it is moderately soluble in amphiphilic media like $\text{CF}_3\text{C}_6\text{H}_5$ and mixtures of benzene and hexafluorobenzene of different ratios.¹⁹

From Table 1 it is clear that the solubility of dppe in

(11) (a) Struder, A.; Curran, D. P. *Tetrahedron* **1997**, *53*, 6681–6696. (b) Struder, A.; Jeger, P.; Wipf, P.; Curran, D. P. *J. Org. Chem.* **1997**, *62*, 2917–2924.

(12) See for example: Brunner, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann W. A., Eds.; VCH: Weinheim, 1996; Chapter 2.2, pp 201–219.

(13) Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Stuart, A. M. *J. Fluorine Chem.* **1999**, *99*, 197–200.

(14) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 4450–4455.

(15) No oxidation products were observed after exposing a toluene solution of **4b** to air for 3 days.

(16) See for example in (a) Casey, C. P.; Paulsen, E.; Beuttenmueller, E. W.; Proft, B. R.; Petrovich, L. M.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 11817–11825. (b) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574–7580. (c) Brunner, H.; Janura, M.; Stefaniak, S. *Synthesis* **1998**, 1742–1749.

(17) For the methylene carbons the sum of $^1J_{\text{PC}}$ and $^2J_{\text{PC}}$ is close to zero, resulting in a singlet (**4a** and **4e**, $^1J_{\text{PC}} + ^2J_{\text{PC}} < 1$ Hz) or a doublet (**3**, $^1J_{\text{PC}} + ^2J_{\text{PC}} = 2$ Hz) for these carbon signals. The *ipso*- and *o*-phenyl carbons are observed as triplets. Satellites on the triplet of the *o*-carbons allowed the determination of $^3J_{\text{PP}}$ (36 Hz) by spectral simulation. No or little second-order effects were observed on the *m*-carbon signals of **4a** and **4e**, whereas a triplet was observed for **3**, indicating a smaller $^3J_{\text{PC}}$ for the former compounds.

(18) King, R. B.; Cloyd, J. C. *J. Chem. Soc., Perkin Trans 2* **1975**, 938–941.

(19) Attempts to synthesize a $(\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2)_2\text{MeSi}$ -substituted derivative of dppe ($n = 2$; $\text{R}_f = \text{C}_8\text{F}_{17}$) gave the desired product. Although its purification was severely hindered by the low solubility, the crude product showed a similar behavior in PFMCH as **4d**.

Table 1. Physical Properties of 4a–e and Dppe

entry	compound				solubility ^a						<i>P</i> ^b	melting range (°C)
					THF		toluene		PFMCH			
	<i>R</i> _f	<i>n</i>	wt % F	(g/L)	(mmol/L)	(g/L)	(mmol/L)	(g/L)	(mmol/L)			
1	dppe	–	–	0	75	188	29	73	– ^c	– ^c	– ^c	134–138
2	4e	–	0	0	162	236	58	85	– ^c	– ^c	0.0 ^d	186–189
3	4a	C ₆ F ₁₃	1	49.0	193	96	14	7	2	1	0.4 ^e	136–138
4	4b	C ₆ F ₁₃	2	59.1	67	20	7	2	>300 ^f	>90 ^f	12	oil
5	4c	C ₆ F ₁₃	3	63.4	11	2	<0.2	<0.04	>300 ^f	>64 ^f	>50 ^g	oil
6	4d ^h	C ₈ F ₁₇	1	53.5	15	6	<0.2	<0.08	1	0.4	– ⁱ	155–159

^a Expressed as the amount of phosphine which can be dissolved in 1 L of pure solvent at 25 °C. Determined by gravimetric methods. (PFMCH = perfluoromethylcyclohexane) ^b In a 1:1 (v/v) mixture of PFMCH and toluene at 0 °C ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$). Determined by gravimetric methods. The estimated error is ± 1 in the last digit. ^c Not determined. ^d No residue was found in the fluororous layer. ^e Clear phase separation was achieved only after 15 h. ^f Both **4b** and **4c** are completely miscible with PFMCH. ^g No residue was found in the toluene layer. ^h Solubility in CF₃C₆H₅ = 14 g/L (5.8 mmol/L). ⁱ Could not be determined due to low solubility in both toluene and PFMCH.

THF and toluene increases upon trimethylsilyl functionalization (entries 1 and 2). Furthermore, the fluororous phase solubility of the diphosphines increases (entries 3–5, *R*_f = C₆F₁₃) while the solubility in THF and toluene decreases (entries 4 and 5) upon attachment of more fluorotails to the phosphine. Compound **4a** has only low solubility in PFMCH, and compounds **4b** and **4c** dissolve well in this fluororous solvent even allowing their purification by fluororous phase extraction (see Experimental Section). Whereas compound **4a** is still highly soluble in THF, **4b** is only moderately soluble and **4c** has low solubility in THF. Compared to the fluororous triphenylphosphine derivatives PAR₃ (Ar = C₆H₄-4-[SiMe₃-*n*(CH₂-CH₂C₆F₁₃)_{*n*}]; *n* = 0–3),^{9c} the solubility of **4b** and **4c** in PFMCH (>300 g/L) is in the same range (*n* = 2: 615 g/L, *n* = 3: 502 g/L).

An important parameter for catalyst recycling by fluororous biphasic extraction is the partition coefficient *P* ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$) of a particular catalytic complex and its fluororous ligands in fluororous biphasic systems. The partition coefficients of **4a–c** and **4e** were determined in a toluene/PFMCH biphasic system and reflect the same trend as their solubility data, i.e., attachment of more perfluoroalkyl tails to the diphosphine leads to an improved affinity for the fluororous phase, resulting in a maximum value for **4c** ($P > 50$ with *n* = 3). In this way, diphosphines differ from the monophosphines PAR₃ (Ar = C₆H₄-4-[SiMe₃-*n*(CH₂CH₂C₆F₁₃)_{*n*}]; *n* = 0–3), where an optimum for *n* = 2 was found.^{9c} This interesting phenomenon will be investigated further in future publications.

Conclusions

Highly fluororous dppe derivatives containing the (CH₂-CH₂)_{*n*}SiMe_{3-*n*} spacer are readily accessible. The flexible synthetic protocol developed, using the Si atom as a branching point, makes this approach particularly useful for parallel synthesis procedures. ³¹P NMR data suggest that the electron density on the phosphorus atom is very similar to the parent compounds dppe and 1,2-bis[bis(4-(trimethylsilyl)phenyl)phosphino]ethane. Therefore, similar coordination chemistry with transition metals is to be expected.

The preferential fluororous phase solubility of the novel fluororous diphosphines increased with the number of tails connected to the silicon atom, resulting in a highest partition coefficient ($P > 50$, in favor of the fluororous phase) for **4c**. Hence, depending on the organic solvent used and the number of fluororous extractions employed,

the fluororous dppe derivatives containing **8** (59.1 wt % F) or **12** perfluoroalkyl tails (63.4 wt % F) (compounds **4b** and **4c**, respectively) are the preferred ligands for fluororous phase metal-catalyzed organic synthetic applications. This aspect is currently under investigation.

Experimental Section

General. All experiments were performed in a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled before use. Fluorinated solvents (c-CF₃C₆F₁₁ (Lancaster), FC-72 and CF₃C₆H₅ (Acros)) were degassed and stored under dinitrogen atmosphere. Fluororous alkylsilyl halides were prepared according to previously reported procedures.^{9,11} Other chemicals were obtained from commercial suppliers (Acros, Aldrich, Lancaster) and used as delivered. Microanalyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mühlheim an der Ruhr. ¹⁹F NMR spectra were externally referenced against C₆F₆ ($\delta = -163$ relative to CFCl₃). The computer program gNMR, version 3.6, Cherwell Scientific Publishing Limited, Oxford, was used for simulation of ¹³C NMR spectra.

1,2-Bis[bis(4-bromophenyl)phosphino]ethane (3). *p*-Dibromobenzene (22.5 g, 95.3 mmol) was dissolved in a mixture of *n*-hexane (300 mL) and diethyl ether (100 mL). To this solution a solution of *n*-BuLi (1.64 M in pentane, 58.1 mL, 95.3 mmol) was added. After stirring for 5 min, the mixture was cooled to –78 °C followed by stirring for another 20 min. To the white suspension was added 1,2-bis(dichlorophosphino)ethane (5.53 g, 23.8 mmol). The reaction mixture was allowed to reach room temperature after 2 h. After stirring the reaction mixture for another 15 h at room temperature, a degassed, saturated aqueous NH₄Cl-solution was added, and the two layers were separated. The aqueous layer was washed with CH₂Cl₂ twice, and the combined organic layers were dried on MgSO₄. Volatiles were evaporated in vacuo to afford **3** (14.46 g, 85%) as a slightly yellow solid. Mp 176–179 °C. ¹H NMR (200 MHz, CDCl₃): δ 1.98 (ps t, *J* = 3.8 Hz, 4H), 7.12–7.43 (m, 16H); ¹³C NMR (50.3 MHz, CDCl₃): δ 24.0 (d, ¹*J*_{PC} + ²*J*_{PC} = 2 Hz), 123.9 (s), 132.0 (t, ³*J*_{PC} = 7 Hz), 134.4 (t, ²*J*_{PC} = 19 Hz), 136.8 (t, ¹*J*_{PC} = 14 Hz); ³¹P NMR (81.0 MHz, CDCl₃): δ –13.8. Anal. Calcd for C₂₆H₂₀-Br₄P₂: C 43.74, H 2.82, P 8.68. Found: C 43.82, H 3.01, P 8.56.

General Procedure for *p*-Silyl-Substituted Dppe Derivatives 4a–e. 1,2-Bis[bis(4-bromophenyl)phosphino]ethane was dissolved in THF and cooled to –90 °C in an ethanol/liquid nitrogen bath. To this solution was added 8 equiv of a solution of *t*-BuLi in pentane. The reaction mixture was stirred for 30 min, while the temperature was kept below –60 °C. The green suspension was treated with 4 equiv of alkylsilyl halide, and the resulting solution was stirred below –60 °C for 1 h. The slightly yellow solution thus formed was warmed to room temperature in 6 h.

4a and 4e. After evaporating all solvents in vacuo, the white solid was dissolved in degassed water/CH₂Cl₂. The organic layer was separated, dried on MgSO₄ and evaporated to dryness. The products were isolated as white solids.

4b and 4c: The residue obtained after evaporating the solvent in vacuo was dissolved in a two-phase system consisting of methanol and FC-72. The fluorour layer was separated and evaporated to dryness, giving a clear yellow oil. The compound was further purified by Kugelrohr (120 °C, 0.1 mbar; **4b**) or washing with pentane (**4c**).

4d: The brownish-white solid, obtained after evaporation of all THF, was washed with degassed water. The suspension was filtered, washed with acetone, and dried in vacuo.

1,2-Bis[bis{4-((2-(perfluorohexyl)ethyl)dimethylsilyl)phenyl}phosphino]ethane (4a). 3 (0.87 g; 1.22 mmol) in THF (20 mL), *t*-BuLi (6.5 mL 1.5 M; 9.8 mmol), and C₆F₁₃CH₂CH₂-SiMe₂Cl (2.26 g; 5.12 mmol) yielded 2.08 g (85%) of a white solid: ¹H NMR (200 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ 0.25 (s, 24H), 0.96 (m, 8H), 2.01–2.12 (m, 12H), 7.22–7.29 (m, 16H); ¹³C NMR (75.5 MHz, toluene-*d*₈): δ -4.1 (s), 5.0 (s), 24.2 (s, ¹J_{PC} + ²J_{PC} < 1 Hz), 26.0 (t, ²J_{FC} = 23.8 Hz), 132.5 (t, ²J_{PC} = 18.3 Hz), 133.6 (m), 137.8 (s), 140.2 (t, ¹J_{PC} = 15.8 Hz); ¹⁹F NMR (282 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -128.2 (m, 2F), -125.1 (m, 2F), -124.9 (m, 2F), -124.0 (m, 2F), -117.9 (m, 2F), -82.8 (m, 3F); ³¹P NMR (81.0 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -11.3. Anal. Calcd for C₆₆H₆₀F₅₂P₂Si₄: C 39.33, H 3.00, P 3.07. Found: C 39.40, H 3.09, P 2.88.

1,2-Bis[bis{4-(di(2-(perfluorohexyl)ethyl)methylsilyl)phenyl}phosphino]ethane (4b). 3 (1.20 g; 1.68 mmol) in THF (30 mL), *t*-BuLi (9.0 mL 1.5 M; 13.5 mmol), and (C₆F₁₃CH₂CH₂)₂-SiMeBr (6.7 g; 6.72 mmol), containing approximately 20 mol % of (C₆F₁₃CH₂CH₂)₂ (determined by ¹H NMR) yielded 4.91 g (87%) of a colorless oil: ¹H NMR (200 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ 0.18 (s, 12H), 0.96 (m, 16H), 2.01 (m, 20H), 7.25 (m, 16H); ³¹P NMR (81.0 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -11.4. Anal. Calcd for C₉₄H₆₄F₁₀₄P₂Si₄: C 33.77, H 1.93, P 1.85. Found: C 33.71, H 1.83, P 1.82.

1,2-Bis[bis{4-(tri(2-(perfluorohexyl)ethyl)silyl)phenyl}phosphino]ethane (4c). 3 (0.47 g; 0.66 mmol) in THF (15 mL), *t*-BuLi (3.5 mL 1.5 M; 5.3 mmol), and (C₆F₁₃CH₂CH₂)₃SiBr (3.58 g; 2.64 mmol), containing approximately 30 mol % of (C₆F₁₃CH₂CH₂)₂ (determined by ¹H NMR) yielded 1.60 g (55%) of a yellow oil: ¹H NMR (200 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ 1.01 (m, 24H), 1.95 (m, 28H), 7.23 (m, 16H); ³¹P NMR (81.0 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -11.4. Anal. Calcd for C₁₂₂H₆₈F₁₅₆P₂Si₄: C 31.37, H 1.47, P 1.33. Found: C 31.46, H 1.38, P 1.44.

1,2-Bis[bis{4-((2-(perfluorooctyl)ethyl)dimethylsilyl)phenyl}phosphino]ethane (4d). 3 (1.15 g; 1.61 mmol) in THF

(20 mL), *t*-BuLi (8.6 mL 1.5 M; 12.9 mmol), and C₈F₁₇CH₂CH₂-SiMe₂Cl (3.49 g; 6.45 mmol) yielded 2.88 g (74%) of a brownish-white solid: ¹H NMR (200 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ 0.23 (s, 24H), 0.94 (m, 8H), 2.03–2.12 (m, 12H), 7.23–7.30 (m, 16H); ¹⁹F NMR (282 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -127.6 (m, 2F), -124.4 (m, 2F), -124.0 (m, 2F), -123.2 (m, 6F), -117.4 (m, 2F), -82.8 (m, 3F); ³¹P NMR (81.0 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -11.3. Anal. Calcd for C₇₄H₆₀F₆₈P₂Si₄: C 36.80, H 2.50, P 2.56. Found: C 36.65, H 2.59, P 2.48.

1,2-Bis[bis{4-(trimethylsilyl)phenyl}phosphino]ethane (4e). 3 (1.26 g; 1.76 mmol) in THF (30 mL), 9.4 mL of a 1.5 M (14.1 mmol) *t*-BuLi solution, and Me₃SiCl (0.80 g; 7.06 mmol) yielded 1.10 g (91%) of a white solid: ¹H NMR (200 MHz, CDCl₃): δ 0.25 (s, 36H), 2.13 (ps t, *J* = 4.4 Hz, 4H), 7.30–7.55 (m, 16H); ¹³C NMR (75.5 MHz, toluene-*d*₈): δ -1.5 (s), 24.6 (s, ¹J_{PC} + ²J_{PC} < 1 Hz), 132.3 (t, ²J_{PC} = 18.3 Hz), 133.3 (s), 139.8 (t, ¹J_{PC} = 15.2 Hz), 140.3 (s); ³¹P NMR (81.0 MHz, C₆D₆/C₆F₆ 1:1 (v:v)): δ -11.4. Anal. Calcd for C₃₈H₅₆P₂Si₄: C 66.42, H 8.21, P 9.01. Found: C 66.51, H 8.28, P 9.06.

Solubility Studies of 4a–e and dppe. Saturated solutions were prepared by stirring the fluorour diphosphine in the appropriate solvent for 30 min at 25 °C. A sample (2.000 ± 0.002 mL) was taken after allowing the mixture to settle, and the mass of this sample was determined. All solvent was removed in vacuo, and the residue was kept under vacuum (0.1 mbar) for 15 h upon which the weight was constant within ± 1 mg, and the weight of the residue was determined.

Determination of Partition Coefficients. A known amount of diphosphine (between 12 and 84 μmol) was dissolved in a biphasic system containing PFMCH (2.000 ± 0.002 mL) and toluene (2.000 ± 0.002 mL). The mixture was stirred until all of the compound had dissolved and then equilibrated in at 0 °C. When two clear layers were obtained, an aliquot (500 ± 2 μL) was removed from each layer by syringe. This was evaporated to dryness, and the residue was kept under vacuum (0.1 mbar) for 15 h upon which the weight was constant within ± 1 mg. Subsequently, the weight of the residue was determined.

Acknowledgment. We thank Elf Atochem Vlissingen B.V. and the Dutch Ministry for Economic Affairs (SENER/BTS) for financial support.

JO000312K