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Syntheses and Properties of Fluorous Quaternary Phosphonium Salts that Bear Four Ponytails; New Candidates for Phase Transfer Catalysts and Ionic Liquids

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Abstract: The fluorous tertiary phosphine $[R_{f6}(CH_2)_2]_3P$ [$R_{fn} = CF_3(CF_2)_{n-1}$] and excess $PhCH_2Br$, $CH_3(CH_2)_3OSO_2CF_3$, or $R_{f6}(CH_2)_2OSO_2CF_3$ react ($CF_3C_6H_5$, 45–110 °C) to give the phosphonium salts $(PhCH_2)[R_{f6}(CH_2)_2]_3P^+ Br^-$ (**2**, 71 %), $[CH_3(CH_2)_3][R_{f6}(CH_2)_2]_3P^+ CF_3SO_3^-$ (**3**, 65 %), or $[R_{f6}(CH_2)_2]_4P^+ CF_3SO_3^-$ (**4**, 83 %). The phosphines $[R_{f6}(CH_2)_2]_2[R_{f8}(CH_2)_2]P$ and $[R_{f8}(CH_2)_2]_3P$ are similarly elaborated with $R_{f6}(CH_2)_2I$, $R_{f8}(CH_2)_2I$, or $R_{f8}(CH_2)_2Br$ (DMF, 115 °C) to $[R_{f8}(CH_2)_2]_{4-x}[R_{f6}(CH_2)_2]_xP^+ I^-$ ($x = 3$, **7**; 2, **8**; 1, **9**; 0, **10**) or $[R_{f8}(CH_2)_2]_4P^+ Br^-$ (80–60 %). The salts exhibit melting points between 110 °C and 43 °C, with lower values favored by less symmetrical cations, R_{f6} segments, and triflate and bromide anions. Solubilities decrease in the solvent sequence $CF_3C_6F_5$ (all salts at least moderately soluble, room temperature) > acetone > THF > $CF_3C_6H_5$ > $CF_3C_6F_{11}$ > $CH_3C_6H_5$, Et_2O, CH_2Cl_2, hexane (all salts insoluble at elevated temperatures); some appreciably increase upon heating. Partition coefficients are very biased towards fluorous phases (>93:<7). The salts can be quite efficient at extracting picrate from water into $CF_3C_6F_5$ (97–86 % for **2**, **4**, **9**, **10**) or $CF_3C_6H_5$ (85–66 % for **2**-**4**), demonstrating their potential for phase transfer catalysis. A $CF_3C_6F_5$ solution of $R_{f8}(CH_2)_3I$ and aqueous NaCl react at 100 °C in the presence (but not the absence) of **9** to give $R_{f8}(CH_2)_3Cl$.

Keywords: fluorous; ionic liquids; phase-transfer catalysis; phosphines; phosphonium salts

Introduction

Among numerous applications, phosphonium salts have attracted considerable recent attention as phase transfer catalysts[1] and ionic liquids.[2,3] Accordingly, there is much interest in the development of new classes of phosphonium salts, and structure/property relationships. For example, over the last decade, a variety of novel phase tags have been developed.[4,5] These represent possible vehicles for realizing phosphonium salts with unusual characteristics. One widely applied phase tag is the fluorous "ponytail",[6] which most commonly has the formula $CF_3(CF_2)_{n-1}(CH_2)_m$ [abbreviated $R_{fn}(CH_2)_m$].

In previous studies, we have reported a variety of syntheses of fluorous aliphatic primary, secondary, and tertiary phosphines bearing $R_{fn}(CH_2)_m$ substituents,[7–10] and related aromatic species.[7,11] Many of the routes to the aliphatic systems are modular in nature, allowing each ponytail to be individually controlled. Horváth, Knochel, and others have reported complementary methodologies.[12–14] We sought to elaborate these phosphines into phosphonium salts with four ponytails. Some other fluorous phosphonium salts are known, as detailed in the discussion section. However, they have either been reported without characterization,[15] or feature at least one nonfluorous substituent (e.g., C_6H_5, CH_2CH_2CN).[13]

In this paper, we describe convenient and easily scaled syntheses of a variety of symmetrically- and unsymmetrically-substituted phosphonium salts that bear three to four ponytails. We furthermore define the liquid ranges of these salts and their solubilities in various solvents, quantify their abilities to transport anions from aqueous to organic solutions, and demonstrate their viability as phase transfer catalysts. Additional details can be found elsewhere.[16]

Results

Syntheses of Fluorous Phosphonium Salts

Two series of syntheses were conducted. The first involved the quaternization of the known symmetrically substituted fluorous tertiary phosphine, $[R_{f6}(CH_2)_2]_3P$ (**1**).[7,8a] Two non-fluorous alkylating agents were studied first to provide reference compounds for the extraction experiments below. As shown in Scheme 1, reactions of **1** with an excess of benzyl bromide ($PhCH_2Br$) or *n*-butyl triflate $[CH_3(CH_2)_3OSO_2CF_3]$ in benzotrifluoride ($CF_3C_6H_5$) at elevated temperatures gave the phosphonium salts $(PhCH_2)[R_{f6}(CH_2)_2]_3P^+$ Br^- (**2**) and $[CH_3(CH_2)_3][R_{f6}(CH_2)_2]_3P^+$ $CF_3SO_3^-$ (**3**) in 71–65% yields after work-up. These and all new phosphorus-containing molecules below were characterized by microanalysis, NMR spectroscopy (^1H, ^{13}C, ^{31}P), and mass spectrometry, as summarized in the Experimental Section. All NMR features were routine.

As shown in Scheme 2 (*top*), **1** and the fluorous primary alkyl triflate $R_{f6}(CH_2)_2OSO_2CF_3$[17] were next reacted. Fluorous alkylating agents are often much less reactive than non-fluorous analogues,[5] and somewhat higher temperatures were required than with *n*-butyl triflate. Work-up gave the symmetrically substituted phosphonium salt $[R_{f6}(CH_2)_2]_4P^+$ $CF_3SO_3^-$ (**4**) in 83% yield.

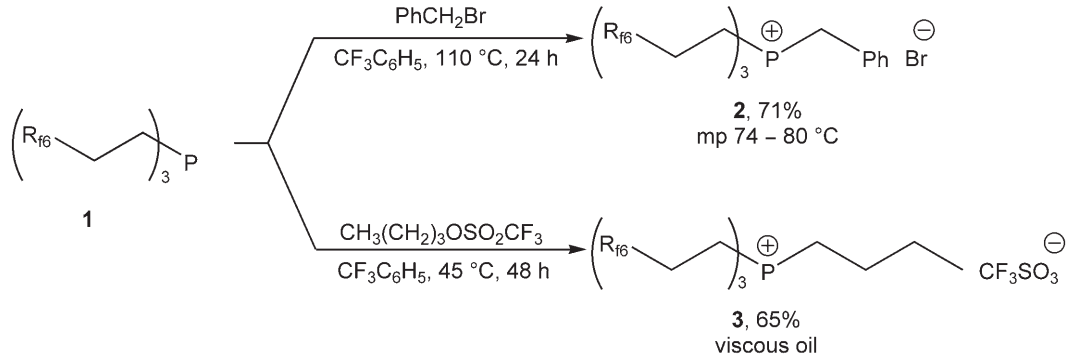
In the second series of syntheses, a family of phosphonium salts with all possible combinations of $R_{f6}(CH_2)_2$ and $R_{f8}(CH_2)_2$ substituents was sought. The unsymmetrically substituted fluorous tertiary phosphine $[R_{f6}(CH_2)_2]_2[R_{f8}(CH_2)_2]P$ (**5**) – prepared as described below – was employed as one starting material. As shown in Scheme 2 (*middle*), reactions with excesses of the fluorous alkyl iodides $R_{fn}(CH_2)_2I$ ($n = 6$, 8) in DMF at 115 °C gave the phosphonium iodides $[R_{f8}(CH_2)_2][R_{f6}(CH_2)_2]_3P^+$ I^- (**7**) and $[R_{f8}(CH_2)_2]_2[R_{f6}(CH_2)_2]_2P^+$ I^- (**8**) in 77–60% yields. Analogous reactions with the symmetrically substituted tertiary phosphine $[R_{f8}(CH_2)_2]_3P$ (**6**)[8a] gave $[R_{f8}(CH_2)_2]_3[R_{f6}(CH_2)_2]P^+$ I^- (**9**) and $[R_{f8}(CH_2)_2]_4P^+$ I^- (**10**) in 80–62% yields.

The fluorous alkyl bromide $R_{f8}(CH_2)_2Br$ has been synthesized from the commercial fluorous alcohol $R_{f8}(CH_2)_2OH$ *via* the tosylate.[18] As shown in Scheme 3 (*top*), we could prepare this bromide directly from the alcohol using CBr_4 and PPh_3.[19] Interestingly, H_2SO_4 and aqueous HBr[20] gave only modest conversions, even at temperatures of >100 °C in sealed vessels. As depicted in Scheme 2 (*bottom*), reaction of the phosphine **6** and an excess of $R_{f8}(CH_2)_2Br$ in DMF at 115 °C gave the symmetrically substituted phosphonium bromide $[R_{f8}(CH_2)_2]_4P^+$ Br^- (**11**) in 79% yield.

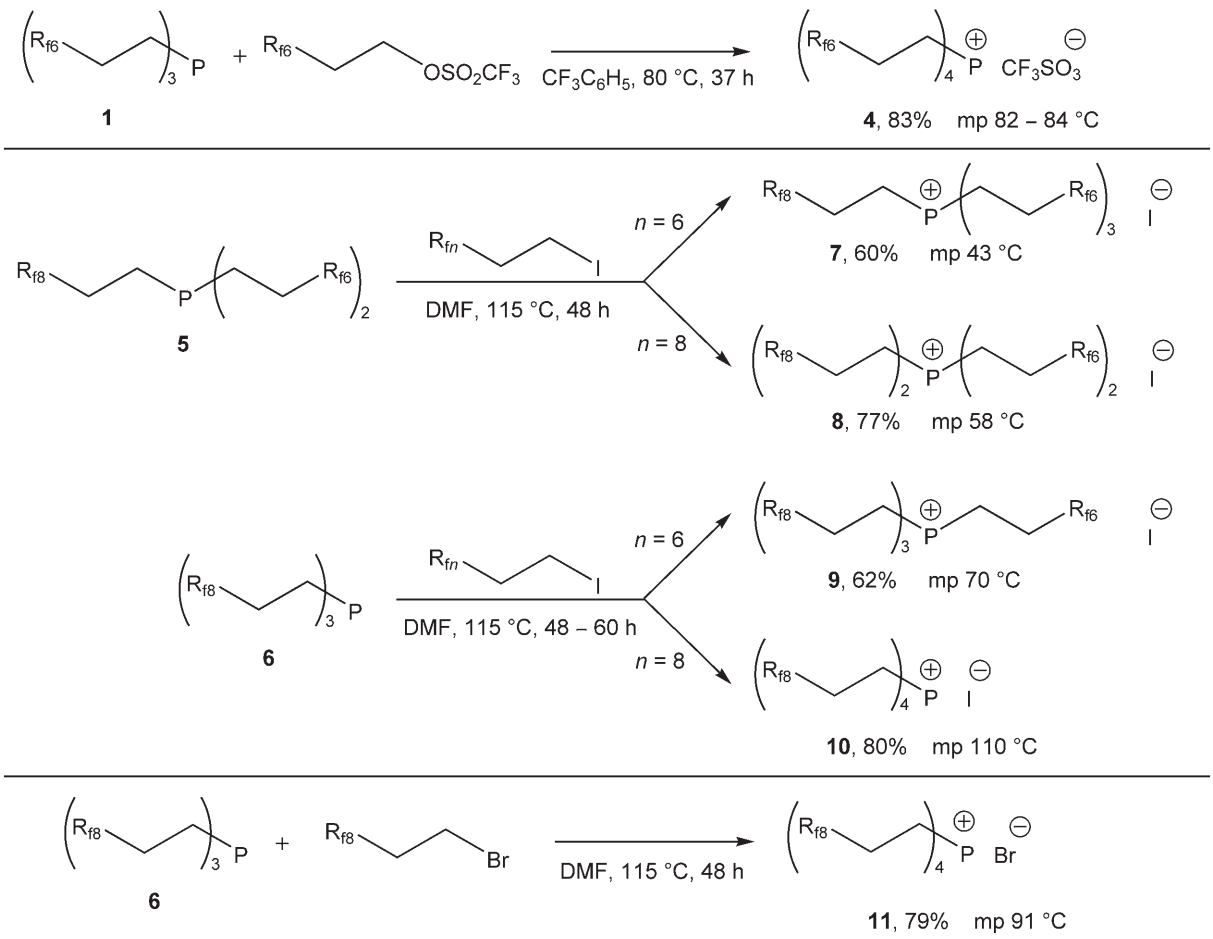
As shown in Scheme 3 (*bottom*), the unsymmetrically substituted phosphine **5** was prepared in 67% yield by free radical chain addition of the fluorous primary phosphine $R_{f8}(CH_2)_2PH_2$ (**12**)[10a] to the commercial fluorous alkene $R_{f6}CH{=}CH_2$. Although **6** is a known compound,[8a] it was also prepared by an analogous reaction of **12** and $R_{f8}CH{=}CH_2$ (65%). Both reactions were easily conducted on 5-gram scales. Since **12** is conveniently synthesized by an Arbuzov/reduction sequence starting with $R_{f8}(CH_2)_2I$,[10a] the somewhat hazardous direct reaction of PH_3 and $R_{f8}CH{=}CH_2$[8a] is avoided.

Phase Properties of Phosphonium Salts

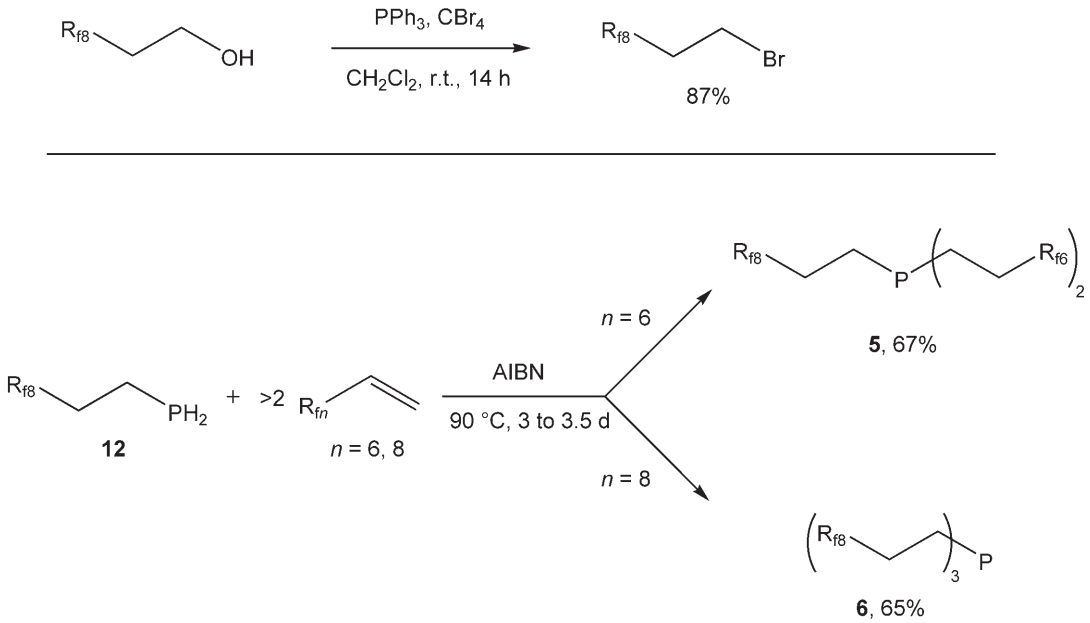
All of the phosphonium salts were obtained as analytically pure solids except for **3**, which was an analytically pure viscous oil. Melting points were determined both conventionally and by DSC for **7**–**11**. As summarized in Scheme 2, values for the salts with four ponytails ranged from 110 °C to 43 °C. The melting points decreased when iodide was replaced by bromide and when R_{f8} segments were replaced by shorter R_{f6} segments. It is well established that ionic liquids with more symmetrical cations exhibit higher melting points than those with less symmetrical cations. Accordingly, the symmetrically substituted phos-



Scheme 1. Syntheses of phosphonium salts with three fluorous substituents.



Scheme 2. Syntheses of phosphonium salts with four fluorous substituents.



Scheme 3. Additional syntheses.

Table 1. Solubility profiles of selected phosphonium salts.[a]

Solvent	Phosphonium salts[b–d]			
	4	**7**	**10**	**11**
$CF_3C_6F_{11}$	sparingly soluble[b] soluble[c]	sparingly soluble[b] soluble[c]	insoluble[b] soluble[c]	insoluble[b] soluble[c]
$CF_3C_6F_5$	very soluble[b,c]	very soluble[b,c]	moderately soluble[b] very soluble[c]	moderately soluble[b] soluble[c]
$CF_3C_6H_5$	very soluble[b,c]	insoluble[b] very soluble[c]	insoluble[b] soluble[c]	insoluble[b] soluble[c]
$CH_3C_6H_5$	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]
acetone	very soluble[b,c]	soluble[b] very soluble[c]	sparingly soluble[b] soluble[c]	insoluble[b] moderately soluble[c]
THF	moderately soluble[b] soluble[c]	moderately soluble[b] soluble[c]	sparingly soluble[b] moderately soluble[c]	insoluble[b,c]
Et_2O	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]
CH_2Cl_2	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]
hexane	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]	insoluble[b,c]

[a] Based upon mass per unit volume and per descriptors in common chemistry handbooks.
[b] 21 °C.
[c] Elevated temperature (4–10 °C below the boiling point of the solvent).
[d] Data for **9**: $CF_3C_6F_5$, soluble,[b] very soluble.[c]

phonium salts **4**, **10**, and **11** show the higher melting points.

As summarized in Table 1, the solubilities of **4**, **7**, **10**, and **11** were assayed in representative solvents at room and elevated temperatures. Solutions could be obtained with the fluorous solvent perfluoro(methylcyclohexane) ($CF_3C_6F_{11}$) at elevated temperatures. The hybrid (ambiphilic)[21] solvent $CF_3C_6H_5$ behaved similarly. Interestingly, perfluorotoluene ($CF_3C_6F_5$) – a non-fluorous or "organic" compound[21] – was the best overall solvent, always giving solutions at room temperature. In most cases, acetone and THF afforded solutions either at room or elevated temperatures. No solubility was observed in hexane, $CH_3C_6H_5$, Et_2O, or CH_2Cl_2 under any conditions. All in all, solubilities decreased with increasing ponytail length, and upon going from triflate to iodide to bromide. The former trend has been observed with many other series of fluorous compounds.[8a]

Selected fluorous/$CH_3C_6H_5$ and fluorous/CH_2Cl_2 partition coefficients were measured as described in the Experimental Section. The data are summarized in Table 2. In the case of **4**, $>96\,\%$ of the salt was found in the fluorous phase employed, perfluoro(1,3-dimethylcyclohexane) [1,3-$(CF_3)_2C_6F_{10}$]. The triply ponytailed phosphonium salt **2** was not very soluble in this solvent. Hence, measurements were conducted in perfluorooctyl bromide [$CF_3(CF_2)_7Br$]. It also exhibited a significant fluorophilicity, with $>93\,\%$ of the salt in the fluorous phase.

Table 2. Partition coefficients of selected phosphonium salts.[a]

Salt	Solvent system	Partition coefficient (%)	Log P
4	1,3-$(CF_3)_2C_6F_{10}$[b]/$CH_3C_6H_5$	96.3/3.7	1.42
4	1,3-$(CF_3)_2C_6F_{10}$[b]/CH_2Cl_2	96.2/3.8	1.40
2	$CF_3(CF_2)_7Br/CH_3C_6H_5$	96.5/3.5	1.44
2	$CF_3(CF_2)_7Br/CH_2Cl_2$	93.9/6.1	1.18

[a] 21 °C.
[b] Perfluoro(1,3-dimethylcyclohexane).

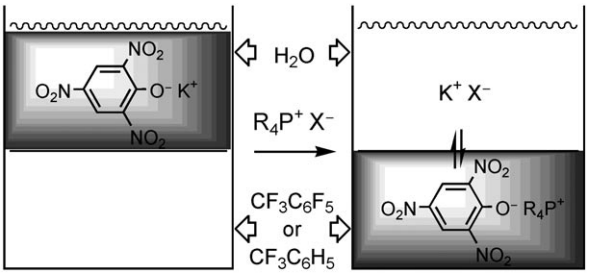
Picrate Extraction Studies

One of the essential roles of a classical phase transfer catalyst is to transfer the inorganic reagent from the aqueous phase into the organic phase, thus enabling the organic substrate to react with the transferred anion and form the product in the organic phase reaction. Before examining applications of the fluorous phosphonium salts in model phase transfer reactions, selected salts were evaluated in potassium picrate extraction experiments[22] in order to define their abilities to transfer picrate from an aqueous phase into a partially fluorinated phase ($CF_3C_6H_5$) and a perfluorinated phase ($CF_3C_6F_5$). As noted above, these are best viewed as hybrid (ambiphilic) and organic (non-fluorous) solvents, respectively.[21]

When either $CF_3C_6H_5$ or $CF_3C_6F_5$ was stirred with an aqueous solution of potassium picrate, the aqueous layer remained bright yellow due to the picrate anion ($\lambda_{max} = 356$ nm) and the organic layer remained colorless. Upon addition of the phosphonium salt, most of the picrate color was transferred into the organic phase. The efficiency of this extraction process was assayed by measuring the decrease of the picrate con-

centration in the aqueous phase using UV-visible spectroscopy. The results are summarized in Table 3.

Table 3. Picrate extractions of selected phosphonium salts.[a]



Phosphonium salt			Picrate extracted [%]	
	R_4P^+	X^-	$CF_3C_6H_5$	$CF_3C_6F_5$
2	$(PhCH_2)[R_{f6}(CH_2)_2]_3P^+$	Br^-	71.8	97.2
3	$[CH_3(CH_2)_3][R_{f6}(CH_2)_2]_3P^+$	$CF_3SO_3^-$	85.0	-
4	$[R_{f6}(CH_2)_2]_4P^+$	$CF_3SO_3^-$	65.8	88.4
9	$[R_{f8}(CH_2)_2]_3[R_{f6}(CH_2)_2]P^+$	I^-	27.5	94.0
10	$[R_{f8}(CH_2)_2]_4P^+$	I^-	25.0	86.2
11	$[R_{f8}(CH_2)_2]_4P^+$	Br^-	37.0	48.9

[a] Equal volumes of a 0.1 mM aqueous solution of potassium picrate and a 0.1 mM $CF_3C_6H_5$ or $CF_3C_6F_5$ solution of the phosphonium salt at 21 °C.

All of the fluorous phosphonium salts performed much better in the water/$CF_3C_6F_5$ biphase than in the water/$CF_3C_6H_5$ biphase because of their higher solubilities in $CF_3C_6F_5$ at room temperature. Excellent picrate extraction levels (97–86%) were obtained for all of the salts, except for the phosphonium bromide **11** (49%), presumably due to its lower solubility in $CF_3C_6F_5$. The order of picrate extraction efficiency in $CF_3C_6F_5$ was $(PhCH_2)[R_{f6}(CH_2)_2]_3P^+$ Br^- (**2**) > $[R_{f8}(CH_2)_2]_3[R_{f6}(CH_2)_2]P^+$ I^- (**9**) > $[R_{f6}(CH_2)_2]_4P^+$ $CF_3SO_3^-$ (**4**) > $[R_{f8}(CH_2)_2]_4P^+$ I^- (**10**) ≫ $[R_{f8}(CH_2)_2]_4P^+$ Br^- (**11**), showing that the bromide, iodide and triflate anions all readily undergo exchange in this system.

The four ponytailed phosphonium salts **9–11** give much lower picrate extraction efficiencies in $CF_3C_6H_5$ (37–25%) than the phosphonium salts **2–4** (85–66%). This is probably due to the much lower solubilities of **9–11** in $CF_3C_6H_5$. The results with **10** and **11** show that bromide undergoes more efficient anion exchange than iodide, despite the lower solubility of the phosphonium bromide **11**.

Phase Transfer Catalysis

A demonstration of the viability of the preceding phosphonium salts as phase transfer catalysts was sought. As shown in Figure 1, a $CF_3C_6F_5$ solution of

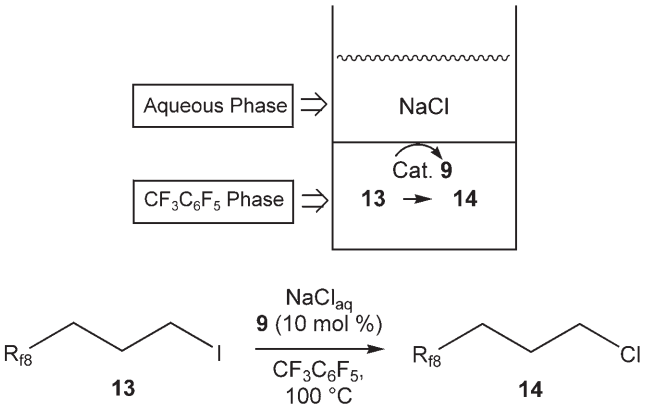


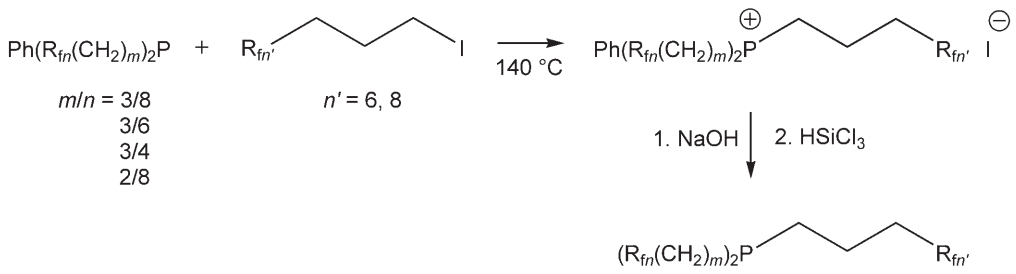
Figure 1. Phase transfer catalysis of a substitution reaction by phosphonium salt **9**.

the fluorous alkyl iodide $R_{f8}(CH_2)_3I$ (**13**) was overlayered with an aqueous NaCl solution (*ca.* 1:10 **13**/NaCl). This educt has one more methylene group than the alkylating agent used in Scheme 2. The phosphonium salt **9** (10 mol%) was added. The sample was stirred at 100 °C in a sealed vial. After 2 h, a ^1H NMR spectrum showed a *ca.* 50:50 mixture of the fluorous alkyl chloride $R_{f8}(CH_2)_3Cl$ (**14**) and **13**. The NaCl solution was replaced with a fresh charge, and the cycle repeated twice (5.5 and 6 h). A ^1H NMR spectrum showed a > 95:< 5 **14**:**13** ratio, with only a trace of **13** detectable. No reaction occurred in the absence of **9**. Hence, **9** can function as a catalyst for phase transfer from aqueous to organic phases.

Discussion

The reactions in Scheme 1 and Scheme 2 nicely establish that fluorous quaternary phosphonium salts consisting of four ponytails are readily available. The precursor phosphines can be prepared on multigram scales, and there is no obvious limit on the scales of the alkylation reactions. Any combination of $R_{fn}(CH_2)_m$ and $R_{fn'}(CH_2)_{m'}$ substituents with $m \geq 2$ should be possible. The salts exhibit excellent thermal and air stabilities, and their yields can likely be further optimized. From the data in Table 2, it can be assumed that partition coefficients will be very biased towards fluorous phases, even when only three ponytails are present.

Horváth has recently described similar sequences starting with phenyl-substituted fluorous phosphines of the formulae $Ph[R_{fn}(CH_2)_m]_2P$ ($m/n = 3/8$, 3/6, 3/4, 2/8).[13b] As shown in Scheme 4, reactions with $R_{fn'}(CH_2)_3I$ ($n' = 6$, 8) were effected in the absence of solvent at 140 °C. Consistent with the preparative goals of this work, the resulting phosphonium salts were dearylated and converted to fluorous tertiary phosphines. Other properties were not investigated.



Scheme 4. Syntheses and reactions of phenyl-substituted fluorous phosphonium salts.

The melting point data in Schemes 1 and 2 indicate that this class of phosphonium salts has particular promise for the development of room temperature ionic liquids. Although it was not a primary objective of this study to minimize melting points, one salt (**3**, Scheme 1) did not solidify at room temperature. Furthermore, by combining the less symmetric cations, as found in **7** and **8**, with more polarizable anions, such as $CF_3SO_3^-$, there seem to be excellent prospects for additional room temperature liquids.

Since fluorous ionic liquids might show specific types of interactions with solutes, they constitute excellent candidates for what have been termed task-specific ionic liquids (TSILs).[23] A variety of ionic liquids are known with short R_{fn} segments ($n < 6$). However, far fewer are known that contain longer R_{fn} segments ($n \geq 6$).[24] A representative series featuring fluorous cations (**15**) is depicted in Figure 2.[24a] An ionic liquid with a fluorous anion (**16**, Figure 2) has been used as a solvent for the homogeneous hydrosilylation of alkenes catalyzed by a fluorous version of Wilkinson's catalyst.[24b]

To our knowledge, there has only been one previous report of a fluorous phase transfer catalyst, the chiral quaternary ammonium salt **17** (Figure 2).[25] This CH_2Cl_2-, $CHCl_3$-, and Et_2O-soluble species has been applied in enantioselective alkylations of activated esters in aqueous/organic biphase systems. Due to its highly fluorous nature, it can be efficiently recycled by extraction with the fluorous solvent FC-72. The perfluoroalkylated 4,13-diaza-18-crown-6 ether **18** (Figure 2) has also been developed recently as a recoverable phase transfer catalyst that promotes aliphatic and aromatic nucleophilic substitutions with iodide and fluoride anions, respectively.[26] It can be recycled six times by fluorous solid phase extraction without any loss in activity.

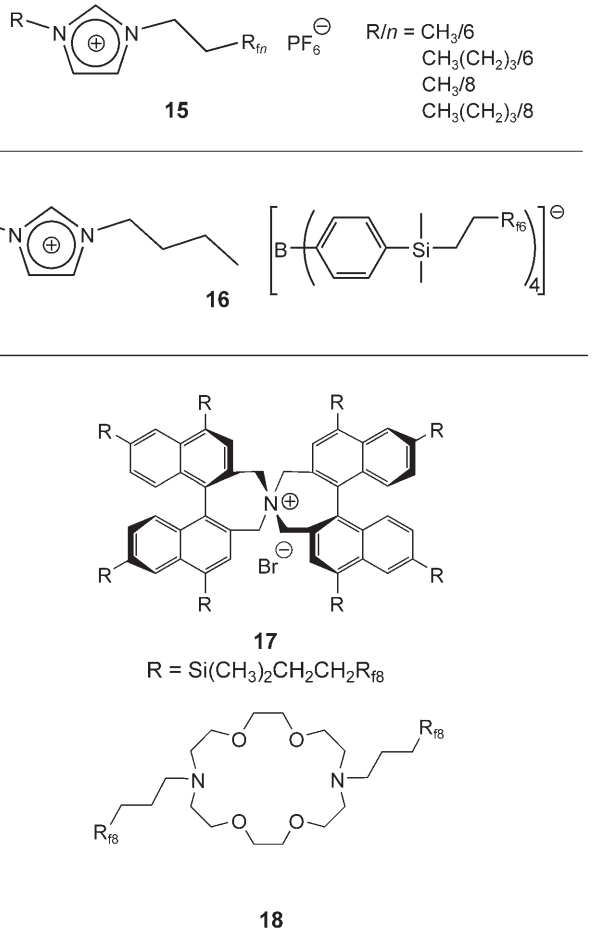


Figure 2. Other fluorous ionic liquids or phase transfer catalysts.

Conclusions

This study has established efficient routes to a variety of symmetrically and unsymmetrically substituted quarternary fluorous phosphonium salts with three and four ponytails. Many of these are low melting solids, and all have high fluorous phase affinities. They efficiently extract picrate ions from aqueous to suitable organic solvents, and their viability as phase transfer catalysts has been demonstrated. Future reports will detail extensions to fluorous arylphosphonium salts,[27] and additional applications in synthesis and catalysis.[28]

Experimental Section

General Remarks

Reactions were conducted under a nitrogen or argon atmosphere unless noted. Chemicals were treated as follows: Et_2O and $CH_3C_6H_5$, distilled from Na/benzophenone; DMF, distilled from CaH_2; hexanes and CH_2Cl_2, simple distillation; $CF_3C_6H_5$ (Fluorochem or ABCR, 99%), distilled, or distilled from P_2O_5, and freeze/pump/thaw degassed (3 ×); $CF_3C_6F_{11}$ (ABCR, 90%) and 1,3-$(CF_3)_2C_6F_{10}$ (Fluorochem, 80+%), distilled from CaH_2; $CF_3(CF_2)_7Br$ (Fluorochem, 98%), simple distillation; $CF_3C_6F_5$ (ABCR or Apollo, 98%), simple distillation; AIBN (Merck, >98%), $R_{f6}CH{=}CH_2$ (Lancaster, 99%), $R_{f8}CH{=}CH_2$ (Apollo, 97%), $R_{f6}(CH_2)_2I$, $R_{f8}(CH_2)_2I$ (2 × Lancaster, 97%), $R_{f6}(CH_2)_2OH$, $R_{f8}(CH_2)_2OH$ (2 × Apollo, 97%), PPh_3, and CBr_4 (2 × Acros, 98%), used as received. The potassium picrate was prepared by the literature procedure using potassium carbonate as the base.[29] Other chemicals or materials were used as received from common commercial sources.

NMR spectra were recorded on Bruker Avance 300 MHz or Jeol GX 400 MHz spectrometers at 27.0 °C in $CDCl_3$, acetone-d_6, $CF_3C_6F_{11}$ or $CF_3C_6F_5$ and referenced as follows: ^{1}H, residual internal $CHCl_3$ ($\delta = 7.24$ ppm) or acetone-d_5 ($\delta = 2.05$ ppm); ^{13}C, internal $CDCl_3$ ($\delta = 77.0$ ppm) or acetone-d_6 ($\delta = 29.92$ ppm); ^{31}P, external H_3PO_4 ($\delta = 0.00$ ppm); ^{19}F, external $CFCl_3$ ($\delta = 0.00$ ppm). The highly coupled ^{13}C signals of the fluorinated carbons are not listed below. Mass spectra were recorded on a Micromass Zabspec instrument. DSC and TGA data were recorded with a Mettler-Toledo DSC821 apparatus and treated by standard methods.[30] Elemental analyses were conducted on a Carlo Erba EA1110 instrument or were performed by the elemental analysis service at the University of North London.

$(PhCH_2)[R_{f6}(CH_2)_2]_3P^+\ Br^-$ (2)

A Schlenk flask was charged with $[R_{f6}(CH_2)_2]_3P$ (**1**; 1.01 g, 0.94 mmol),[7] $PhCH_2Br$ (0.96 g, 5.65 mmol), and $CF_3C_6H_5$ (10 mL), and then freeze/pump/thaw/degassed. The sample was stirred at 110 °C for 24 h and cooled. The solvent was removed by rotary evaporation. The viscous oil was triturated with hexane and $CH_3C_6H_5$. The salt was dried under oil pump vacuum and washed with Et_2O. The Et_2O was decanted and the residue was dried by oil pump vacuum to give **2** as a white solid; yield: 0.82 g (0.66 mmol, 71%); mp 74–80 °C (capillary); anal. calcd. for $C_{31}H_{19}BrF_{39}P$: C 29.94, H 1.54, P 2.49, Br 6.43; found: C 29.46, H 1.45, P 2.10, Br 6.17; ^{1}H NMR (acetone-d_6): $\delta = 7.95$ (m, 2H, Ph*H*), 7.71 (m, 3H, Ph*H*), 5.13 (d, $^2J_{HP} = 15.8$ Hz, 2H, PhCH_2), 3.60 (m, 6H, CH_2CH_2P), 3.19 (m, 6H, CF_2CH_2); ^{1}H{^{31}P} NMR (acetone-d_6): $\delta = 7.80$ (m, 2H, Ph*H*), 7.48 (m, 3H, Ph*H*), 5.13 (s, 2H, PhCH_2), 3.60 (m, 6H, CH_2CH_2P), 3.19 (m, 6H, CF_2CH_2); ^{13}C{^{1}H} NMR (acetone-d_6): $\delta = 130.8$, 130.7, 129.8 (3 d, $J_{CP} = 6$, 3, 4 Hz, *p*/*m*/*o*-Ph), 129.5 (d, $^2J_{CP} = 9$ Hz, *i*-Ph), 27.2 (d, $^1J_{CP} = 44$ Hz, PhCH_2), 25.0 (t, $^2J_{CF} = 22$ Hz, CF_2CH_2), 12.5 (d, $^1J_{CP} = 51$ Hz, CH_2CH_2P); ^{31}P NMR (acetone-d_6): $\delta = 36.9$ (s); ^{19}F{^{1}H} NMR (acetone-d_6): $\delta = -80.85$ (m, 9F, CF_3), −114.25 (t, $^4J_{FF} = 13.9$ Hz, 6F, CF_2CH_2), −121.50 (m, 6F, CF_2), −122.56 (m, 12F, 2 × CF_2), −125.91 (m, 6F, CF_2); MS (positive FAB, 3-NBA): $m/z = 1164$ ($[M-Br]^+$, 100%); MS (negative FAB, 3-NBA): $m/z = 79/81$ (Br^-, 100%).

$[CH_3(CH_2)_3][R_{f6}(CH_2)_2]_3P^+\ CF_3SO_3^-$ (3)

The compounds $CH_3(CH_2)_3OSO_2CF_3$ (0.60 g, 2.9 mmol), **1** (0.50 g, 0.47 mmol) and $CF_3C_6H_5$ (5 mL) were combined in a procedure analogous to that for **2** and stirred at 45 °C for 48 h. An identical work-up gave **3** as a viscous oil; yield: 0.39 g (0.31 mmol, 65%); anal. calcd. for $C_{29}H_{21}F_{42}O_3PS$: C 27.24, H 1.66; found: C 27.36, H 1.52; ^{1}H NMR (acetone-d_6): $\delta = 3.20$ (m, 6H, $CF_2CH_2CH_2P$), 2.99–2.84 (m, 8H, CF_2CH_2, $CH_2CH_2CH_2P$), 1.86 (m, 2H, CH_2CH_2P), 1.58 (m, 2H, CH_3CH_2), 0.98 (t, $^3J_{HH} = 7.7$ Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (acetone-d_6): $\delta = 23.4$ (d, $^3J_{CP} = 19$ Hz, CH_3CH_2), 23.3 (t, $^2J_{CF} = 19$ Hz, CF_2CH_2), 22.9 (d, $J_{CP} = 5$ Hz, $CH_3CH_2CH_2$), 17.6 (d, $^1J_{CP} = 46$ Hz, $CH_2CH_2CH_2P$), 12.5 (s, CH_3), 10.6 (d, $^1J_{CP} = 52$ Hz, $CF_2CH_2CH_2P$); ^{31}P NMR (acetone-d_6): $\delta = 40.0$ (s); ^{19}F{^{1}H NMR} (acetone-d_6): $\delta = -77.92$ (s, 3F, CF_3SO_3), −80.81 (m, 9F, CF_3), −114.23 (t, $^4J_{FF} = 14.4$ Hz, 6F, CF_2CH_2), −121.50 (m, 6F, CF_2), −122.53 (m, 12F, 2 × CF_2), −125.86 (m, 6F, CF_2); MS (positive FAB, 3-NBA): $m/z = 1129$ ($[M-OSO_2CF_3]^+$, 100%); MS (negative FAB, 3-NBA): $m/z = 149$ ($CF_3SO_3^-$, 100%).

$[R_{f6}(CH_2)_2]_4P^+\ CF_3SO_3^-$ (4)

The compounds $R_{f6}(CH_2)_2OSO_2CF_3$ (1.83 g, 3.69 mmol),[17] **1** (0.40 g, 0.37 mmol), and $CF_3C_6H_5$ (3 mL) were combined in a procedure analogous to that for **2** and stirred at 80 °C for 37 h. The solvent was removed by rotary evaporation, and the excess $R_{f6}(CH_2)_2OSO_2CF_3$ by Kugelrohr distillation under reduced pressure. The oily solid was triturated with $CH_3C_6H_5$ and CH_2Cl_2. The residue was dried by oil pump vacuum to give **4** as a white solid; yield: 0.48 g (0.31 mmol, 83%); mp 82–84 °C (capillary); anal. calcd. for $C_{33}H_{16}F_{55}O_3PS$: C 25.27, H 1.03, P 1.97, S 2.04; found: C 25.28, H 1.04, P 2.47, S 2.05; ^{1}H NMR (acetone-d_6): $\delta = 3.37$ (m, 8H, CH_2P), 3.11 (m, 8H, CF_2CH_2); ^{13}C{^{1}H} NMR (acetone-d_6): $\delta = 23.5$ (t, $^2J_{CF} = 23$ Hz, CF_2CH_2), 10.8 (d, $^1J_{CP} = 52$ Hz, CH_2P); ^{31}P NMR (acetone-d_6): $\delta = 42.4$ (s); ^{19}F{^{1}H} NMR (acetone-d_6): $\delta = -78.22$ (s, 3F, OSO_2CF_3), −80.84 (m, 12F, CF_3), −114.11 (t, $^4J_{FF} = 13.3$ Hz, 8F, CF_2CH_2), −121.51 (m, 8F, CF_2), −122.59 (m, 16F, 2 × CF_2), −125.88 (m, 8F, CF_2); MS (positive FAB, 3-NBA): $m/z = 1419$ ($[M-OSO_2CF_3]^+$, 100%); MS (negative FAB, 3-NBA): $m/z = 149$ ($CF_3SO_3^-$, 100%).

$[R_{f8}(CH_2)_2][R_{f6}(CH_2)_2]_2P$ (5)

A round-bottom flask was fitted with an N_2 inlet and a condenser and charged with $R_{f8}(CH_2)_2PH_2$ (**12**;[10a] 2.925 g, 6.095 mmol), $R_{f6}CH{=}CH_2$ (7.632 g, 22.05 mmol), AIBN (0.120 g, 0.731 mmol), and $CH_3C_6H_5$ (7.0 mL). The solution

was stirred at 90 °C for 36 h. A ^{31}P NMR spectrum of an aliquot showed that **12** was consumed, but that some intermediate secondary phosphine remained. The sample was cooled and the solvent removed by oil pump vacuum. Another charge of $R_{f6}CH{=}CH_2$ (4.219 g, 12.19 mmol) and AIBN (0.120 g, 0.731 mmol) was added. The mixture was stirred at 90 °C for 48 h. The sample was cooled and the volatiles removed by oil pump vacuum. The yellow-brown oil was filtered through SiO_2 (13 g; Ø 3.3 cm) with $CF_3C_6H_5$ (300 mL). The solvent was removed by oil pump vacuum and the light yellow oil distilled (Kugelrohr) to give **5** as a colorless oil; yield: 4.766 g (4.066 mmol, 67 %); bp 220 °C/0.06 torr; anal. calcd. for $C_{26}H_{12}F_{43}P$: C 26.64, H 1.03; found: C 26.28, H 1.12; ^{1}H NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): $\delta = 2.13$ (m, 6H, CH_2P), 1.66 (m, 6H, CF_2CH_2); ^{13}C{^{1}H} 27.6 (dt, $^2J_{CP} = 20$ Hz, $^2J_{CF} = 22$ Hz, CF_2CH_2), 16.5 (d, $^1J_{CP} = 17$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): $\delta = -25.1$ (s); MS (positive FAB, 3-NBA: $m/z =$ 1189 ($[M+H+O]^+$, 100 %), 1172 ($[M]^+$, 74 %), 1153 ($[M-F]^+$, 21 %).

$[R_{f8}(CH_2)_2]_3P$ (6)[8a]

The phosphine **12** (2.499 g, 5.206 mmol), $R_{f8}CH{=}CH_2$ (8.402 g, 18.83 mmol), AIBN (0.103 g, 0.625 mmol), and $CH_3C_6H_5$ (6.0 mL) were combined in a procedure analogous to that for **5** (90 °C, 48 h; second charge of $R_{f8}CH{=}CH_2$ (4.645 g, 10.41 mmol) and AIBN (0.103 g, 0.625 mmol); 100 °C, 24 h). The sample was cooled and the volatiles removed by oil pump vacuum. The pale yellow solid was filtered through SiO_2 (26 g; Ø 3.5 cm) with $CF_3C_6H_5$ (300 mL). The solvent was removed by oil pump vacuum and the solid recrystallized from $CF_3C_6H_5$ (14 mL). This gave **6** as a white solid; yield: 4.653 g (3.391 mmol, 65 %); mp 51 °C (capillary), 50 °C (DSC, T_e); anal. calcd. for $C_{30}H_{12}F_{51}P$: C 26.26, H 0.88; found: C 25.89, H 0.97. ^{1}H NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): $\delta = 2.11$ (m, 6H, CH_2P), 1.61 (m, 6H, CF_2CH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): $\delta = 28.1$ (dt, $^2J_{CP} = 20$ Hz, $^2J_{CF} = 23$ Hz, CF_2CH_2), 17.0 (d, $^1J_{CP} = 17$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): $\delta = -25.1$ (s); MS (positive FAB, 3-NBA): $m/z = 1389$ ($[M+H+O]^+$, 100 % vs. peaks with $m/z < 1450$), 1373 ($[M+H]^+$, 80 %), 1354 ($[M+H-F]^+$, 20 %).

$[R_{f8}(CH_2)_2][R_{f6}(CH_2)_2]_3P^+ I^-$ (7)

A 4 mL vial was charged with $R_{f6}(CH_2)_2I$ (0.4247 g, 0.8959 mmol), **5** (0.3500 g, 0.2986 mmol), and DMF (1.5 mL), and tightly sealed. The sample was vigorously stirred at 115 °C for 48 h and cooled. The upper colorless DMF layer was separated from the lower dark brown fluorous layer. The latter was dried under oil pump vacuum and triturated with Et_2O. The Et_2O was decanted and the residue dried by oil pump vacuum to give **7** as a yellow solid; yield: 0.2947 g (0.1791 mmol, 60 %); mp 50 °C (capillary), 43 °C (DSC, T_e); TGA: onset of a 93 % mass loss 196.5 °C; anal. calcd. for $C_{34}H_{16}F_{56}IP$: C 24.81, H 0.98; found: C 24.91, H 1.11; ^{1}H NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 3.45$ (m, 8H, CH_2P), 2.81 (m, 8H, CF_2CH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 24.2$ (t, $^2J_{CF} = 24$ Hz, CF_2CH_2), 12.8 (d, $^1J_{CP} = 54$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 40.4$ (s); MS (positive FAB, 3-NBA): $m/z = 1519$ ($[M-I]^+$, 100 %).

$[R_{f8}(CH_2)_2]_2[R_{f6}(CH_2)_2]_2P^+ I^-$ (8)

DMF (1.5 mL), $R_{f8}(CH_2)_2I$ (0.1797 g, 0.3131 mmol), and **5** (0.1223 g, 0.1044 mmol) were combined in a procedure analogous to that for **7**. An identical work-up gave **8** as a yellow solid; yield: 0.1411 g (0.0808 mmol, 77 %); mp 64 °C (capillary), 58 °C (DSC, T_e); TGA: onset of a 93 % mass loss 203.5 °C; anal. calcd. for $C_{36}H_{16}F_{60}IP$: C 24.76, H 0.92; found: C 24.84, H 1.05; ^{1}H NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 3.48$ (m, 8H, CH_2P), 2.86 (m, 8H, CF_2CH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 24.2$ (t, $^2J_{CF} = 24$ Hz, CF_2CH_2), 12.9 (d, $^1J_{CP} = 51$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 40.5$ (s); MS (positive FAB, 3-NBA): = 1619 ($[M-I]^+$, 100 %).

$[R_{f8}(CH_2)_2]_3[R_{f6}(CH_2)_2]P^+ I^-$ (9)

DMF (1.5 mL), $R_{f6}(CH_2)_2I$ (0.2073 g, 0.4374 mmol), and **6** (0.3000 g, 0.2187 mmol) were combined in a procedure analogous to that for **7**. An identical work-up gave **9** as a light brown solid; yield: 0.2498 g (0.1353 mmol, 62 %); mp 75 °C (capillary), 70 °C (DSC, T_e); TGA: onset of a 89 % mass loss 197.3 °C; anal. calcd. for $C_{38}H_{16}F_{64}IP$: C 24.72, H 0.87; found: C 24.99, H 0.90; ^{1}H NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 3.51$ (m, 8H, CH_2P), 2.87 (m, 8H, CF_2CH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 24.4$ (t, $^2J_{CF} = 22$ Hz, CF_2CH_2), 13.0 (d, $^1J_{CP} = 53$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 40.5$ (s); MS (positive FAB, 3-NBA): $m/z = 1719$ ($[M-I]^+$, 100 %).

$[R_{f8}(CH_2)_2]_4P^+ I^-$ (10)

DMF (1.5 mL), $R_{f8}(CH_2)_2I$ (0.4184 g, 0.7289 mmol), and **6** (0.5000 g, 0.3644 mmol) were combined in a procedure analogous to that for **7**. An identical work-up gave **10** as a light brown solid; yield: 0.5681 g (0.2919 mmol, 80 %); mp 110 °C (capillary), 110 °C (DSC, T_e); TGA: onset of a 92 % mass loss 209.8 °C; anal. calcd. for $C_{40}H_{16}F_{68}IP$: C 24.68, H 0.83; found: C 24.73, H, 0.80; ^{1}H NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 3.46$ (m, 8H, CH_2P), 2.86 (m, 8H, CF_2CH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 24.2$ (t, $^2J_{CF} = 24$ Hz, CF_2CH_2), 12.8 (d, $^1J_{CP} = 52$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 40.4$ (s); MS (positive FAB, 3-NBA): $m/z = 1818$ ($[M-H-I]^+$, 100 %).

$[R_{f8}(CH_2)_2]_4P^+ Br^-$ (11)

DMF (1.5 mL), $R_{f8}(CH_2)_2Br$ (0.2776 g, 0.5268 mmol), and **6** (0.1807 g, 0.1317 mmol) were combined in a procedure analogous to that for **7**. An identical work-up gave **11** as a beige

solid; yield: 0.1981 g (0.1043 mmol, 79%); mp 91 °C (capillary), 91 °C (DSC, T_e); TGA: onset of a 91% mass loss 209.5 °C; anal. calcd. for $C_{40}H_{16}BrF_{68}P$: C 25.30, H 0.85; found: C 25.29, H 0.89; ^{1}H NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 3.54$ (m, 8H, CH_2P), 2.94 (m, 8H, CF_2CH_2); $^{13}C\{^1H\}$ NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 24.1$ (t, $^2J_{CF} = 23$ Hz, CF_2CH_2), 12.5 (d, $^1J_{CP} = 51$ Hz, CH_2P); ^{31}P NMR ($CF_3C_6F_5$ + $CDCl_3$ capillary): $\delta = 40.3$ (s); MS (positive FAB, 3-NBA): $m/z = 1819$ ($[M-Br]^+$, 100%).

$R_{f8}(CH_2)_2Br$[31]

A flask was charged with $R_{f8}(CH_2)_2OH$ (4.01 g, 8.61 mmol), PPh_3 (2.46 g, 9.41 mmol), and CH_2Cl_2 (30 mL), and cooled in an ice bath. A solution of CBr_4 (3.12 g, 9.41 mmol) in CH_2Cl_2 (5 mL) was added with stirring. The mixture was allowed to warm to room temperature. After 14 h, the solvent was removed by rotary evaporation, and pentane (40 mL) was added. The mixture was filtered (removing PPh_3/$OPPh_3$ and starting alcohol), and the filtrate was concentrated by rotary evaporation. Chromatography (short SiO_2 column, hexanes) gave $R_{f8}(CH_2)_2Br$ as a colorless oil; yield: 3.98 g (7.55 mmol, 87%); anal. calcd for $C_{10}H_4BrF_{17}$: C 22.79, H 0.77; found: C 22.86, H 0.94; ^{1}H NMR ($CDCl_3$): $\delta = 3.39$ (t, $^3J_{HH} = 8$ Hz, 2H, CH_2Br), 2.67–2.49 (m, 2H, CF_2CH_2); $^{13}C\{^1H\}$ ($CDCl_3$): $\delta = 35.0$ (t, $^2J_{CF} = 22$ Hz, CF_2CH_2), 20.1 (t, $^3J_{CF} = 6$ Hz, CH_2Br).

Phase Transfer Catalysis[31]

A 4 mL vial was charged with $R_{f8}(CH_2)_3I$ (**13**;[32] 0.1274 g, 0.2167 mmol), **9** (0.0400 g, 0.0217 mmol), $CF_3C_6F_5$ (0.5 mL) and aqueous NaCl (0.5 mL, 5 M, 2.5 mmol), tightly sealed, and vigorously stirred at 100 °C. After 2 h, the mixture was cooled. A ^{1}H NMR spectrum of an aliquot from the organic phase ($CDCl_3$) showed a *ca.* 50:50 ratio of $R_{f8}(CH_2)_3Cl$ (**14**) and **13**. The aqueous phase was removed and fresh aqueous NaCl (0.5 mL, 5 M) added. The sample was vigorously stirred at 100 °C for 5.5 h and cooled (NMR, *ca.* 83:17 **14**/**13**). The aqueous phase was similarly renewed and the sample vigorously stirred at 100 °C for 6 h and cooled (NMR, > 95:< 5 **14**/**13**).

Compound **14**: ^{1}H NMR ($CF_3C_6F_5$ + $CDCl_3$): $\delta = 3.60$ (t, $^3J_{HH} = 7$ Hz, 2H, CH_2Cl), 2.36–2.04 (2 m, 4H, $CF_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 43.5$ (s, CH_2Cl), 28.5 (t, $^2J_{CF} =$ 21 Hz, CF_2CH_2), 23.6 (t, $^3J_{CF} = 6$ Hz, CH_2CH_2Cl). An independent synthesis and additional data will be reported shortly.[28]

Partition Coefficients (Table 2)

The organic solvent (4 mL) and the fluorous solvent (Table 2; 4 mL) were added to a vial containing the phosphonium salt (0.050–0.100 g) and a magnetic stir bar. The samples were stirred at 21 °C for 0.5 h and allowed to stand for 0.5 h for the phases to separate. An aliquot was removed from each phase (2 mL). The solvent was removed and the residue dried under oil pump vacuum (0.01 mm Hg) and then weighed.

Potassium Picrate Extractions (Table 3)

Equal volumes of a $CF_3C_6H_5$ or $CF_3C_6F_5$ solution of the phosphonium salt (10 mL, 0.1 mM; if necessary, the samples were warmed to dissolve the salt) and aqueous potassium picrate (0.1 mM) were introduced into a stoppered flask and stirred for 0.5 h at 21 ± 1 °C. The sample was allowed to stand for 2 h at the same temperature to allow complete phase separation. The absorbance of the picrate in the aqueous phase was measured at 356 nm with a Shimadzu UV-visible spectrophotometer. The percentage of picrate extracted into the non-aqueous phase was calculated by:

$$\%\ \text{Extraction} = 100\ (\text{Abs}_{\text{before}} - \text{Abs}_{\text{after}})/\text{Abs}_{\text{before}}$$

where $\text{Abs}_{\text{before}}$ is the absorbance of a similarly diluted sample of the unextracted potassium picrate solution and $\text{Abs}_{\text{after}}$ is the absorbance of the potassium picrate solution after extraction. Three independent extractions were performed for each combination of potassium picrate and ionophore, and the results were averaged.

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