Additions of PH_3 to Monosubstituted Alkenes of the Formula $H_2C{=}CH(CH_2)_x(CF_2)_yCF_3$: Convenient, Multigram Syntheses of a Family of Partially Fluorinated Trialkylphosphines with Modulated Electronic Properties and Fluorous Phase Affinities

Luke J. Alvey, Drew Rutherford, Jerrick J. J. Juliette, and J. A. Gladysz*,†

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received April 14, 1998

Reactions of PH_3 and commercially available $H_2C{=}CHR_f$ ($R_{f6/8/10} = (CF_2)_5CF_3/(CF_2)_7CF_3/(CF_2)_9CF_3$) give, in two-stage processes conducted with free radical initiators (AIBN, VAZO; 80−90 °C), the phosphines $P(CH_2CH_2R_f)_3$ (**1**−**3**; 63−75%). Analogous reactions with $H_2C{=}CHCH_2R_{f8}$ (**7**) and $H_2C{=}CHCH_2CH_2R_{f8}$ (**10**) give $P(CH_2CH_2CH_2R_{f8})_3$ (**4**, 73%) and $P(CH_2CH_2CH_2CH_2R_{f8})_3$ (**5**, 66%), in which the phosphorus is increasingly insulated from the electronegative R_f moiety. The alkenes **7** and **10** are prepared from $Bu_3SnCH_2CH{=}CH_2$ and IR_{f8} ($h\nu$, CH_2Cl_2, 81%) or ICH_2R_{f8} (VAZO, refluxing $CF_3C_6H_5$, 56%). The reaction of **1** and H_2O_2 gives $O{=}P(CH_2CH_2R_{f6})_3$ (**6**, 88%), which can be reduced with $HSiCl_3$ to **1**. Partition coefficients ($CF_3C_6F_{11}$/toluene, 27 °C) range from 98.8:1.2 (**1**, **4**) through 98.9:1.1 (**5**) to >99.7:<0.3 (**2**, **3**, **6**). Crystals of **4** diffract poorly, but a packing motif that maximizes interactions between R_f segments is evident.

One of the most innovative new approaches to catalysis involves perfluorinated or "fluorous"[1−3] solvents such as perfluoroalkanes, perfluoroethers, and perfluoroamines. As detailed in a series of articles by Horváth,[1,2] this protocol exploits the temperature-dependent miscibility of fluorous and organic solvents. Many combinations afford bilayers at room temperature, but one phase at higher temperatures. Accordingly, catalysts that have high affinities for fluorous media offer unique possibilities. As shown in Figure 1, they may react under homogeneous conditions in the high temperature monophasic limit and easily be recovered in the low-temperature biphasic limit. This design element combines the best features of homogeneous and heterogeneous catalysts.[4a]

To achieve high fluorous phase affinities, Horváth proposed that catalysts be derivatized with "pony tails"—substituents such as $(CH_2)_x(CF_2)_yCF_3$.[1] The perfluoroalkyl or $R_{f(y+1)}$ segments serve, when of sufficient length and number, a "like dissolves like" function. Furthermore, the $(CH_2)_x$ "spacer" segments can provide tuning elements. At higher values of *x*, the reaction center will be insulated from the electron withdrawing $R_{f(y+1)}$ moieties. At lower values, the Lewis acidity will be enhanced. Phosphines would constitute an obvious testing ground for this concept, since there are a large number of important processes that utilize metal phosphine complexes as catalysts,[4b] as well as many reactions catalyzed by phosphines alone.[5]

In separate and collaborative investigations, we and Horváth have shown that rhodium complexes containing the partially fluorinated trialkylphosphine $P(CH_2CH_2(CF_2)_5CF_3)_3$ or "$P(CH_2CH_2R_{f6})_3$" (**1**) catalyze a variety of transformations, have high affinities for fluorous media, and can be easily recovered and recycled.[1,6−8] In this paper, we describe convenient, large scale preparations of **1** and homologues in which the six-carbon perfluoroalkyl segment is lengthened (**2**, R_{f8}; **3** R_{f10}). We also describe syntheses of homologues in which the $(CH_2)_2$ spacer segment is lengthened (**4**, $(CH_2)_3R_{f8}$; **5**, $(CH_2)_4R_{f8}$). The resulting series of phosphines (Chart 1) features gradually modulated donor strengths, as well as fluorous phase affinities. Together, they constitute a valuable "toolkit" for the systematic development of catalytic reactions based upon fluorous trialkylphosphines or their metal complexes.

Other results reported below include (1) the synthesis and reduction of the fluorous phosphine oxide $O{=}P(CH_2CH_2R_{f6})_3$ (**6**), (2) partition coefficients that quantify the affinities of **1**−**6** for fluorous media, and (3) partial crystallographic data for **4**. Additional syntheses of **1** have been described by other investigators,[9] and alternative routes to fluorous trialkylphosphines developed in our laboratory will be detailed separately.[10] Metal triarylphosphine catalysts that feature one pony tail per

† New address: Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany.

(1) (a) Horváth, I. T.; Rabái, J. *Science* **1994**, *266*, 72. (b) Horváth, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rabái, J.; Mozeleski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133.

(2) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 1, in press.

(3) Additional perspectives: (a) Gladysz, J. A. *Science* **1994**, *266*, 55. (b) Studer, A.; Hadida, S.; Ferritto, R.; Kim, S.-Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823. (c) Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2057; *Angew. Chem.* **1997**, *109*, 2147.

(4) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH Publishers: New York, 1996. See (a) Vol. 2, Ch. 3.1.1. (b) Vol. 1, Ch. 2.2, 2.3, 2.5, 2.6, 2.9.

(5) Representative examples: (a) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001. (b) Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 3836.

(6) (a) Juliette, J. J. J.; Horváth, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1610; *Angew. Chem.* **1997**, *109*, 1682. (b) Juliette, J. J. J.; Rutherford, D.; Horváth, I. T.; Gladysz, J. A., manuscript in preparation.

(7) Rutherford, D.; Juliette, J. J. J.; Rocaboy, C.; Horváth, I. T.; Gladysz, J. A. *Catal. Today* **1998**, *42*, 381.

(8) Dinh, L., unpublished results, University of Utah.

(9) (a) Benefice-Malouet, S.; Blancou, H.; Commeyras, A. *J. Fluorine Chem.* **1985**, *30*, 171. (b) Langer, F.; Püntener, K.; Stürmer, R.; Knochel, P. *Tetrahedron: Asymmetry* **1997**, *8*, 715. (c) Battacharyya, P.; Gudmunsen, D.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Stuart, A. M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3609.

S0022-3263(98)00692-6 CCC: $15.00
Published on Web 09/04/1998

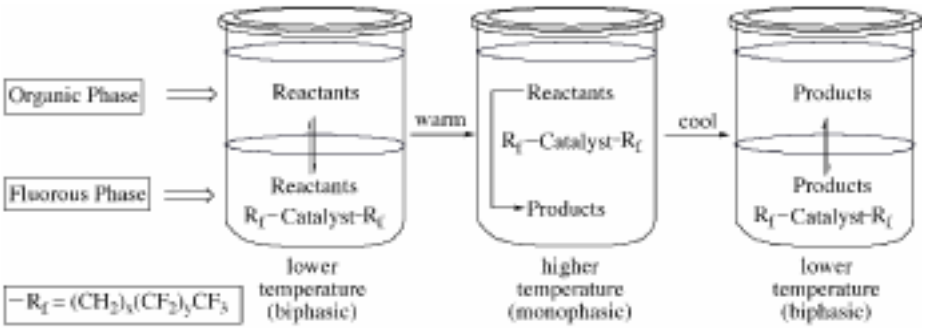
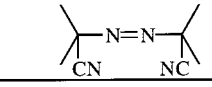
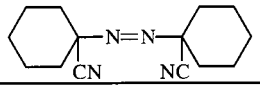


Figure 1. One possibility for catalysis with fluorous solvents.

Chart 1. Summary of Abbreviations

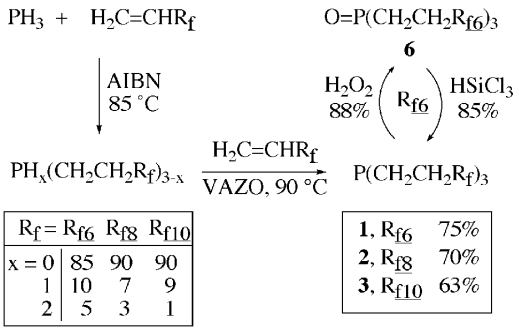
Compound	Abbreviation
$P(CH_2CH_2(CF_2)_5CF_3)_3$	$P(CH_2CH_2R_{f6})_3$ (**1**)
$P(CH_2CH_2(CF_2)_7CF_3)_3$	$P(CH_2CH_2R_{f8})_3$ (**2**)
$P(CH_2CH_2(CF_2)_9CF_3)_3$	$P(CH_2CH_2R_{f10})_3$ (**3**)
$P(CH_2CH_2CH_2(CF_2)_7CF_3)_3$	$P(CH_2CH_2CH_2R_{f8})_3$ (**4**)
$P(CH_2CH_2CH_2CH_2(CF_2)_7CF_3)_3$	$P(CH_2CH_2CH_2CH_2R_{f8})_3$ (**5**)
$O=P(CH_2CH_2(CF_2)_5CF_3)_3$	$O=P(CH_2CH_2R_{f6})_3$ (**6**)
	AIBN
	VAZO

aryl ring have also recently been reported,[11] as well as a number of fluorous catalysts that are not phosphine based.[12]

Results

1. Reactions of PH_3 and $H_2C{=}CHR_f$. Free radical chain additions of phosphorus−hydrogen bonds to alkenes are well-known.[13] Since many alkenes of the formula $H_2C{=}CHR_f$ are commercially available, this represents an obvious approach to the title compounds. Indeed, a preliminary study of the reaction of PH_3 gas[14] and $H_2C{=}CHR_{f6}$ was found to give the fluorous phosphine **1** in 26% yield.[1a] The synthesis was conducted at 100 °C in an autoclave in the presence of the initiator AIBN (Chart 1). Small amounts of primary and secondary phosphine byproducts, $PH_2(CH_2CH_2R_{f6})$ and $PH(CH_2CH_2R_{f6})_2$, were removed by a second AIBN charge.

Scheme 1. Syntheses of Fluorous Phosphines with $(CH_2)_2$ Spacers



$R_f = R_{f6}$	R_{f8}	R_{f10}
x = 0	85	90	90
1	10	7	9
2	5	3	1

1, R_{f6}	75%
2, R_{f8}	70%
3, R_{f10}	63%

This lead was adapted to the syntheses summarized in Scheme 1. Key design considerations were as follows: (1) a $PH_3/H_2C{=}CHR_f$ stoichiometry of approximately 1:3 was employed, (2) temperatures of 80−85 °C were used to moderate the rate of AIBN decomposition,[15] (3) the initial mixture of primary, secondary, and tertiary phosphines was treated with a second alkene charge (4−20% of the first charge) and the less reactive initiator VAZO.[15] It was thought that slower initiation rates might minimize any independent polymerization of the alkene, which is at higher concentration than PH_3 after the first charge and may be in excess over phosphorus−hydrogen bonds after the second charge.

Gratifyingly, analytically pure 4−8 g quantities of the $CH_2CH_2R_{f6}$, $CH_2CH_2R_{f8}$, and $CH_2CH_2R_{f10}$ substituted phosphines **1**−**3** could be isolated in 63−75% yields based upon the total alkene utilized. Since **1**−**3** constitute 85−90% of the crude phosphine products after the first alkene charge, comparable yields might be possible at that stage. However, complicated or tedious workups would likely be required. The phosphines **1**−**3** showed progressive increases in melting points (liquid, 47−48 °C, 102−103 °C) and decreases in $CF_3C_6F_{11}$ solubilities. No other phase transitions were evident by DSC. Needles of **2** could be grown from $CF_3C_6H_5$/toluene, but were unfortunately too thin for crystallography. All compounds survived vacuum distillation, and mass spectra (EI) exhibited intense molecular ions.

(10) Alvey, L. J.; Bernatis, P. B., unpublished results, University of Utah, and manuscripts in preparation.

(11) (a) Betzemeier, B.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2623; *Angew. Chem.* **1997**, *109*, 2736. (b) See also Kainz, S.; Baumann, W.; Koch, D.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628; *Angew. Chem.* **1997**, *109*, 1699.

(12) (a) Klement, I.; Lütjens, H.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1454; *Angew. Chem.* **1997**, *109*, 1605. (b) Vincent, J.-M.; Rabion, A.; Yachandra, V. K.; Fish, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2346; *Angew. Chem.* **1997**, *109*, 2438. (c) Ryu, I.; Niguma, T.; Minakata, S.; Komatsu, M.; Hadida, S.; Curran, D. P. *Tetrahedron Lett.* **1997**, *38*, 7883. (e) Pozzi, G.; Cinato, F.; Montanari, F.; Quici, S. *J. Chem. Soc., Chem. Commun.* **1998**, 877.

(13) (a) Gilheany, D. G.; Mitchell, C. M. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley & Sons: New York, 1990; Vol. 1, p 173. (b) Rauhut, M. M.; Currier, H. A.; Semsel, A. M.; Wystrach, V. P. *J. Org. Chem.* **1961**, *26*, 5138. (c) Hackney, M. L. J.; Schubert, D. M.; Brandt, P. F.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1997**, *36*, 1867 and references therein. (d) Baxley, G. T.; Miller, W. K.; Lyon, D. K.; Miller, B. E.; Nieckarz, G. F.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 6688.

(14) **Caution**: PH_3 (bp −87.7 °C) is toxic and hazardous and must be handled in strict accordance with the safety literature. Spontaneous room temperature ignition normally requires traces of P_2H_4: (a) *Dictionary of Inorganic Compounds*; Chapman & Hall: New York, 1992; Vol. 3, p 3386. (b) Toy, A. D. F. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, 1973; Vol. 2, p 414. (c) *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley & Sons: New York, 1994; Vol. 6, p 3160.

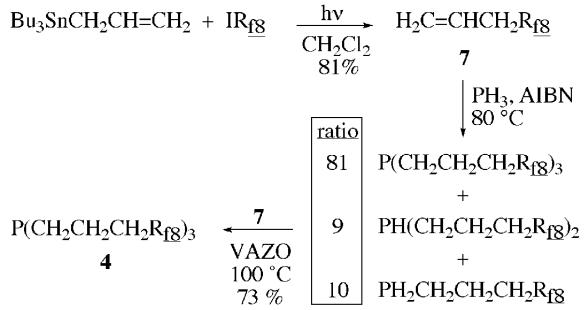
(15) Ravve, A. *Principles of Polymer Chemistry*; Plenum Press: New York, 1995; p 38.

The NMR properties of **1**−**3** were similar, with little variation due to the lengths of the R_f segments (e.g., $^{31}P\{^1H\}$, δ −25.5 to −25.4, $CF_3C_6F_{11}$). The $^{13}C\{^1H\}$ spectra showed P***C***H_2 signals that were coupled to phosphorus but not, within detection limits, to fluorine (δ 16.5−16.4, $^1J_{CP}$ = 16−17 Hz, $w_{1/2}$ = 8.0−8.6 Hz). The $PCH_2\boldsymbol{C}H_2CF_2$ signals were downfield (δ 27.6−27.4, $^2J_{CP}$ = 20−21 Hz; $^2J_{CF}$ = 23−24 Hz) and strongly coupled to both phosphorus and fluorine. The ^{31}P NMR signals of the primary and secondary phosphine byproducts (Scheme 1) showed the expected multiplicities and chemical shift trends.[16] To ensure accurate ratios, T_1 measurements were made and appropriate spectral parameters utilized.[16]

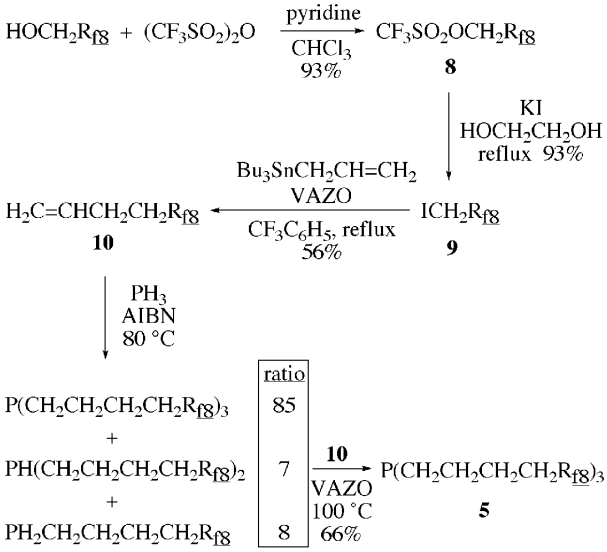
2. Syntheses and Reactions of $H_2C{=}CH(CH_2)_{x-2}R_{f8}$. Tri(*n*-octyl)phosphine contains the same number of carbon atoms as **1**, but lacks fluorine atoms. Thus, it constitutes a valuable reference. Iridium carbonyl derivatives, *trans*-Ir(Cl)(CO)$(L)_2$, of both phosphines have been characterized.[17] The IR $\nu_{C=O}$ value is significantly higher for the adduct of **1** (1975 vs 1942 cm^{-1}). Hence, the $(CH_2)_2$ spacers do not completely insulate the iridium from the electron-withdrawing R_{f6} groups. Accordingly, we sought to extend the preceding syntheses to phosphines with longer $(CH_2)_x$ segments. This in turn requires alkenes with CH_2 groups between the vinyl and R_f moieties.

Such alkenes do not appear to be commercially available. However, free radical chain additions of perfluoroalkyl iodides (IR_f) to alkenes are well-known.[18] Furthermore, allyl stannanes are frequently used to effect free radical chain allylations.[19] It has been reported that ICF_3 and IR_{f6} react with the allyl stannane $Bu_3SnCH_2CH{=}CH_2$ in the presence of a palladium(0) initiator to give alkenes of the formula $H_2C{=}CHCH_2R_f$.[20] Accordingly, IR_{f8} and $Bu_3SnCH_2CH{=}CH_2$ were photolyzed as shown in Scheme 2. Workup gave $H_2C{=}CHCH_2R_{f8}$ (**7**), which has been prepared previously by different routes,[21] in 81% yield on a 12−13 g scale. Then PH_3 and **7** were reacted in a sequence similar to those in Scheme 1. The phosphine **4**, which features $(CH_2)_3$ spacer segments, was isolated as an analytically pure white powder in 73% yield on a 4−5 g scale.

Scheme 2. Synthesis of a Fluorous Phosphine with $(CH_2)_3$ Spacers



Scheme 3. Synthesis of a Fluorous Phosphine with $(CH_2)_4$ Spacers



A phosphine with still longer spacer segments was sought. Accordingly, the commercially available alcohol $HOCH_2R_{f8}$ was converted to the corresponding triflate **8** in 93% yield as shown in Scheme 3.[22] The modest electrophilicity of **8** as compared to other triflates was evidenced by its stability to an aqueous workup. Reaction of **8** and KI in refluxing $HOCH_2CH_2OH$ gave the iodide ICH_2R_{f8} (**9**) in 93% yield on a 25 g scale. A thermal reaction with $Bu_3SnCH_2CH{=}CH_2$, using VAZO as the initiator, afforded the alkene $H_2C{=}CHCH_2CH_2R_{f8}$ (**10**)[23] in 56% yield on a 5 g scale. Then PH_3 and **10** were reacted in a sequence similar to those in Scheme 1. The phosphine **5**, which features $(CH_2)_4$ spacer segments, was isolated as an analytically pure white powder in 66% yield on a 4 g scale.

The phosphines **4** and **5** were characterized identically to **1**−**3** above. Together with **2**, they define another homologous series ($(CH_2)_xR_{f8}$, x = 2, 3, 4). They became more air sensitive as x increases, consistent with an attenuated electron-withdrawing effect of the R_{f8} group. However, the melting points did not follow an obvious

(16) (a) The following T_1 values were measured with standard software: **5**, $T_1 = 1.66 \pm 0.01$ s; $PH(CH_2CH_2CH_2CH_2R_{f8})_2$ $T_1 = 1.47 \pm 0.04$ s; $PH_2CH_2CH_2CH_2CH_2R_{f8}$ $T_1 = 2.94 \pm 0.07$ s. Accordingly, phosphine ratios were determined using a 45° pulse width, a 10 s relaxation delay, and a 1.6 s acquisition time. Data for experiments in Schemes 1−3 follow. (b) **1** (85.2%, δ −25.5), $PH(CH_2CH_2R_{f6})_2$ (9.6%, δ −67.0, d, $^1J_{HP}$ = 198 Hz), $PH_2CH_2CH_2R_{f6}$ (5.2%, δ −140.8, t, $^1J_{HP}$ = 190 Hz). (c) **2** (89.7%, δ −25.4), $PH(CH_2CH_2R_{f8})_2$ (7.4%, δ −67.1, d, $^1J_{HP}$ = 200 Hz), $PH_2CH_2CH_2R_{f8}$ (2.9%, δ −141.0, t, $^1J_{HP}$ = 192 Hz). (d) **3** (90.4%, δ −25.5), $PH(CH_2CH_2R_{f10})_2$ (8.7%, δ −67.1, d, $^1J_{HP}$ = 199 Hz), $PH_2CH_2CH_2R_{f10}$ (0.9%, δ −141.0, t, $^1J_{HP}$ = 193 Hz). (e) **4** (80.9%, δ −34.8), $PH(CH_2CH_2CH_2R_{f8})_2$ (9.1%, δ −73.4, d, $^1J_{HP}$ = 193 Hz), $PH_2CH_2CH_2CH_2R_{f8}$ (10.0%, δ −145.5, t, $^1J_{HP}$ = 190 Hz). (f) **5** (85.1%, δ −32.8), $PH(CH_2CH_2CH_2CH_2R_{f8})_2$ (6.8%, δ −70.9, d, $^1J_{HP}$ = 194 Hz), $PH_2CH_2CH_2CH_2CH_2R_{f8}$ (8.1%, δ −140.8, t, $^1J_{HP}$ = 190 Hz).

(17) (a) Guillevic, M.-A.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1612; *Angew. Chem.* **1997**, *109*, 1685. (b) Guillevic, M.-A.; Rocaboy, C.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Organometallics* **1998**, *17*, 707.

(18) (a) Brace, N. O.; Marshall, L. W.; Pinson, C. J.; van Wingerden, G. *J. Org. Chem.* **1984**, *49*, 2361; Huang, W.-Y.; Zhang, H.-Z. *J. Fluorine Chem.* **1990**, *50*, 133. (b) Feiring, A. E. *J. Org. Chem.* **1985**, *50*, 3269.

(19) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley: M. R. *Tetrahedron* **1985**, *41*, 4079.

(20) Matsubara, S.; Mitani, M.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 5857.

(21) Earlier syntheses: (a) Umemoto, T.; Kuriu, Y. *Tetrahedron Lett.* **1981**, *22*, 5197. (b) Umemoto, T.; Kuriu, Y.; Nakayama, S.-i. *Tetrahedron Lett.* **1982**, *23*, 1169. (c) Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 307. (d) Hu, C.-M.; Qing, F.-L.; Huang, W.-Y. *J. Org. Chem.* **1991**, *56*, 2801. (e) Améduri, B.; Boutevin, B.; Nouiri, M.; Talbi, M. *J. Fluorine Chem.* **1995**, *74*, 191. (f) Yamamoto, Y.; Saito, K. *Organometallics* **1997**, *16*, 2207. (g) Napoli, M.; Gambaretto, G. P. *J. Fluorine Chem.* **1997**, *84*, 101.

(22) This compound has been described in patents in the following Chemical Abstracts citations: (a) Hansen, R. L. **1967**, *67*, 63788. (b) Masahiro, I. **1994**, *121*, 280253. (c) Masahiro, I. **1995**, *122*, 105246.

(23) This compound has been described once previously in a patent. Chemical Abstracts citation: Meinert, H. **1997**, *126*, 250892.

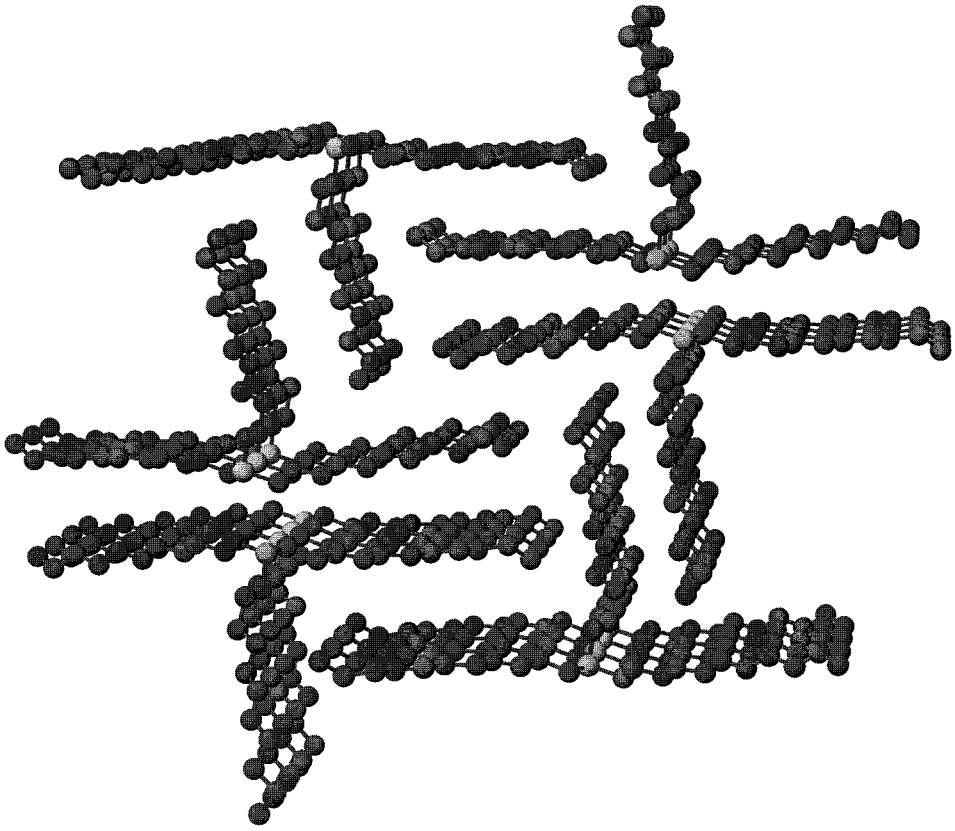


Figure 2. Packing diagram for $P(CH_2CH_2CH_2(CF_2)_7CF_3)_3$ (**4**).

trend (47−48 °C, 71.5−72.5 °C, 44.5−45.0 °C). No other phase transitions were evident by DSC. The solubilities in toluene progressively increased (**2**, sparingly soluble near reflux; **5**, very soluble at room temperature). Surprisingly, the ^{31}P NMR chemical shifts did not exhibit a monotonic trend (δ −25.5, −34.8, −32.8). The ^{13}C NMR signals of the CH_2 groups were assigned from the J_{CP}, $^1J_{CH}$, and J_{CF} values (Experimental Section) and shifted downfield with increasing proximity to the R_{f8} moiety.

3. Other Reactions or Characterization. As we studied the preceding phosphines and their metal complexes, decomposition products believed to be phosphine oxides were sometimes observed. Accordingly, an authentic sample was sought. As shown in Scheme 1, **1** was treated with H_2O_2, which is often used to convert phosphines to phosphine oxides.[24a] Workup gave the expected product $O{=}P(CH_2CH_2R_{f6})_3$ (**6**) in 88% yield as an analytically pure white powder. Consistent with literature precedent, the ^{31}P NMR chemical shift was downfield of that of **1** (δ 41.2 vs −25.5). The CH_2 ^{13}C NMR signals exhibited chemical shifts and J_{CF} values comparable to those of **1**, but J_{CP} values that were much different (δ 19.3, d, $^1J_{PC}$ = 68 Hz; 24.2, t, $^2J_{CF}$ = 24 Hz).

We also sought methods for the reduction of fluorous phosphine oxides. Following an established protocol,[24b,25] **6** and excess $HSiCl_3$ were reacted at 48 °C. As shown in Scheme 1, workup gave **1** in 85% yield. However, NMR analysis of the crude product showed traces of $PH(CH_2CH_2R_{f6})_2$ that were not in the original sample, as well as other unidentified species.

When hot toluene solutions of **4** were stored at 27 °C, single crystals formed. Although they diffracted poorly, data sets were collected using CCD detectors. These could not be refined to suitable levels for bond length and angle analyses. However, the packing motif was also of interest, and a diagram is provided in Figure 2 (key data, −75 °C: $P2_1/n$, $Z = 4$, unit cell ca. 23.06 × 6.46 × 32.49 Å). Although each phosphorus is pyramidal, from one perspective the three pony tails define a T-shape. When viewed from the plane of the "T", infinite stacks are evident. The horizontal part of each "T" defines a "raft". These pack back-to-back ("T" under "⊥") along an orthogonal axis. Along the remaining axis, there are parallel contacts between the vertical stems of "T"+"⊥" pairs. Hence, **4** packs in a manner that maximizes fluorous contacts in every dimension.

Finally, $CF_3C_6F_{11}$/toluene partition coefficients for **1**−**6** were carefully measured by GLC as described in the Experimental Section. Data are summarized in Table 1. Interestingly, a small amount of **1** can reproducibly be detected in the toluene phase. However, the higher homologues **2** and **3** do not detectably partition into the toluene phase. Importantly, integrations of solvent impurity peaks indicate that amounts less than 0.3% might not be detected. Other trends are analyzed below.

Discussion

There is now an extensive literature on fluorinated phosphines.[26] However, most examples feature *per*fluo-

(24) (a) Bhattacharya, A. K.; Roy, N. K. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley & Sons: New York, 1992; Vol. 2, p 197. (b) Gilheany, D. G.; Mitchell, C. M. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley & Sons: New York, 1990; Vol. 1, p 167.

(25) Symmes, C., Jr.; Quin, L. D. *J. Org. Chem.* **1976**, *41*, 238.

(26) Schnabel, R. C.; Roddick, D. M. *ACS Symp. Ser.* **1994**, *55*, 421 and references therein.

Table 1. Partition Coefficients (27 °C)[a]

analyte	$CF_3C_6F_{11}$/toluene
$P(CH_2CH_2R_{f6})_3$ (**1**)	98.8:1.2[b]
$P(CH_2CH_2R_{f8})_3$ (**2**)	>99.7:<0.3
$P(CH_2CH_2R_{f10})_3$ (**3**)	>99.7:<0.3
$P(CH_2CH_2CH_2R_{f8})_3$ (**4**)	98.8:1.2[c]
$P(CH_2CH_2CH_2CH_2R_{f8})_3$ (**5**)	98.9:1.1[d]
$O{=}P(CH_2CH_2R_{f6})_3$ (**6**)	>99.7:<0.3

[a] Derived from the average of 3−11 GLC injections as described in the Experimental Section. All ratios were confirmed by a second independent determination (agreement to ±0.1). [b] 98.8(0.5):1.2(0.5). [c] 98.8(0.4):1.2(0.4). [d] 98.9(0.3):1.1(0.3).

roalkyl or *per*fluoroaryl substituents. Although some of these may possess appreciable affinities for fluorous media, they were usually prepared in conjunction with programs directed at new highly π acidic ligands. As such, they should be poor substitutes for the good donor phosphines employed in most metal-catalyzed reactions. Nonetheless, they may be useful as replacements for π acidic carbon monoxide ligands, thus affording fluorous derivatives of metal carbonyl catalysts.

To our knowledge, trialkylphosphines of the formula $P((CH_2)_x(CF_2)_7CF_3)_3$ are unknown prior to this work. Other syntheses of **1**, or derivatives thereof, have been described previously.[9] The first preparation, reported in 1985 but often overlooked in citation lists and literature surveys, utilized PCl_3 and the fluorous iodozinc reagent $IZnCH_2CH_2R_{f6}$.[9a] While our work was in progress, Knochel found that the reaction of PCl_3 with the dialkyl zinc reagent $Zn(CH_2CH_2R_{f6})_2$ and then $BH_3{\cdot}SMe_2$ gives the borane adduct $\mathbf{1}{\cdot}BH_3$ in 75% yield.[9b] Finally, the reaction of PCl_3 with the Grignard reagent $IMgCH_2CH_2R_{f6}$ has been reported to give **1** in 50% yield.[9c]

These routes avoid the hazards associated with PH_3.[14] On the other hand, the generation of the fluorous zinc or Grignard reagents requires the iodide $ICH_2CH_2R_{f6}$[9] or an organoborane derived from the alkene $H_2C{=}CHR_{f6}$.[9b] Our procedures are more direct and superior from the standpoint of atom economy. We also spent considerable effort trying to prepare **4** and **5** from PCl_3 and the corresponding Grignard or alkyllithium reagents.[10] However, success was limited.

Nolan has probed the steric and electronic properties of **1** calorimetrically.[27] Experiments with $[Rh(CO)_2Cl]_2$ show that **1** is a poorer donor than $P(CH_2CH_3)_3$, and a comparable donor to $P(C_6H_5)(CH_3)_2$. This indicates, consistent with other data above, that the $(CH_2)_2$ spacers do not completely insulate the phosphorus from the R_{f6} groups. Experiments with $(\eta^5\text{-}C_5R_5)Ru(COD)(Cl)$ (R = H, CH_3) suggest a cone angle of 130° ± 4°, close to that of $P(CH_2CH_3)_3$ (132°). We anticipate that **1**−**5** will be comparable sterically, and that **1**−**3** will be comparable electronically. However, as evidenced by the trend in air sensitivity, **4** and **5** are progressively more electron releasing.

To our knowledge, only a few partition coefficients involving organic compounds and fluorous and organic phases have been measured.[7,28] The data in Table 1 reveal high fluorous phase affinities and several conspicuous trends. First, as the lengths of the R_f segments increase in the series **1**−**3**, the partition coefficients increase from 98.8:1.2 to >99.7:<0.3. This illustrates the applicability of the "like dissolves like" paradigm, and the possibilities for rational design. The actual coefficients for **2** and **3** may be higher, but the amounts remaining in the organic phase are subject to detection limits as described above.

However, it should be emphasized that the *absolute* solubilities of **1**−**3** in $CF_3C_6F_{11}$ progressively decrease. We find similar phenomena with non-phosphorus-containing fluorous compounds. Since the partition coefficients or *relative* $CF_3C_6F_{11}$/toluene solubilities increase in the series **1**−**3**, there must be an even steeper decrease in toluene solubilities. Such solubility decreases are common as molecules approach macromolecular limits. Another noteworthy trend involves **2**, **4**, and **5**. As the $(CH_2)_x$ spacer segment is lengthened, detectable quantities of the phosphine are again found in the nonfluorous phase. These compounds also exhibit a marked accompanying increase of absolute solubilities in toluene. Interestingly, the phosphine oxide **6** has a higher partition coefficient than the corresponding phosphine **1**.

The partition coefficients of **1**, **4**, and **5** are sufficiently high that they could be viewed as "immobilized" with respect to many laboratory applications. However, they would slowly leach under some conditions and not meet the most rigorous industrial end-use criteria. In this regard, we believe it is essential for researchers developing fluorous catalysts or reagents to report careful partition coefficient measurements. As noted above, fluorous attributes have been claimed for triarylphosphines in which each aryl group bears a single pony tail.[11] However, arylphosphine substituents should, relative to the alkyl substituents **1**−**3**, significantly enhance organic phase affinities.

In summary, we have developed convenient large scale syntheses of a family of approximately isosteric fluorous trialkylphosphines, $P((CH_2)_x(CF_2)_yCF_3)_3$, which feature modulated electronic properties and fluorous phase affinities. Syntheses of additional types of fluorous phosphines, as well as further applications in catalysis, will be reported soon.

Experimental Section

General. All reactions and workups were conducted under inert atmospheres unless noted. Solvents were employed as follows: $CF_3C_6F_{11}$, $CF_3C_6H_5$, $CHCl_3$, distilled from P_2O_5; CH_2Cl_2, distilled from CaH_2; toluene, hexanes, benzene, ether, distilled from Na/benzophenone; pyridine, distilled from Na; ethylene glycol, dried over $MgSO_4$ (24 h); C_6D_6, $CDCl_3$ (Cambridge Isotope Laboratories), used as received. Reagents were utilized as follows: PH_3 (Scott Specialty Gases),[14] used as received; $H_2C{=}CH(CF_2)_5CF_3$, $H_2C{=}CH(CF_2)_7CF_3$, $H_2C{=}CH(CF_2)_9CF_3$ (Oakwood/Fluorochem), freeze−pump−thaw degassed (5×); $ICF_2(CF_2)_6CF_3$ (PCR), used as received; $HOCH_2(CF_2)_7CF_3$ (PCR), dried over $MgSO_4$; $Bu_3SnCH_2CH{=}CH_2$, AIBN, VAZO, H_2O_2 (Aldrich), used as received; $(CF_3SO_2)_2O$ (Aldrich), distilled from P_2O_5; KI, dried over P_2O_5 (100 °C, drying pistol, 24 h); $HSiCl_3$ (ROC/RIC), vacuum transferred. Silica gel (Merck, grade 9385, 230−400 mesh) was dried under vacuum (3×10^{-3} mmHg, 180 °C, 24 h). Instrumental data and NMR spectra with resonance assignments are provided as Supporting Information.

$P(CH_2CH_2(CF_2)_5CF_3)_3$ (1). A test tube (80 × 150 mm) was charged with $H_2C{=}CH(CF_2)_5CF_3$ (6.902 g, 19.94 mmol), AIBN

(27) Li, C.; Nolan, S. P.; Horváth, I. T. *Organometallics* **1998**, *17*, 452.

(28) (a) Solé-Violan, L.; Devallez, B.; Postel, M.; Riess, J. G. *New J. Chem.* **1993**, *17*, 581. (b) Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286.

(0.302 g, 1.84 mmol, 9 mol %), and a Teflon stir bar and placed in a tube-shaped stainless steel bomb (30 cm^3 volume). The bomb was sealed and connected to a PH_3 tank. The assembly was evacuated and filled with N_2 (3×), and evacuated and pressurized with PH_3 (75 psi, ca. 6.3 mmol).[14,29] The bomb was partially immersed in an oil bath (80−85 °C), and the contents were stirred. Every 4 h, the bomb was repressurized from 45−60 psi to 75 psi (ca. 2 mmol). After 22 h, the bomb was vented, purged with N_2 (1 h), transferred into a glovebox, and opened. An aliquot of the dark orange viscous oil was dissolved in $CF_3C_6F_{11}$. A ^{31}P NMR spectrum showed a mixture of $PH_{3-n}(CH_2CH_2(CF_2)_5CF_3)_n$ (Scheme 1).[16b] A ^1H NMR spectrum showed traces of alkene. Then $CF_3C_6H_5$ (5 mL), VAZO (0.255 g, 1.04 mmol), and $H_2C{=}CH(CF_2)_5CF_3$ (1.00 g, 2.89 mmol) were added to the oil. The mixture was kept in a Schlenk flask at 90 °C for 24 h, and darkened. The solvent was removed by oil pump vacuum to give a white solid suspended in orange liquid. Then $CF_3C_6F_{11}$ (20 mL) and toluene (20 mL) were added. The layers were separated. Volatiles were removed from the $CF_3C_6F_{11}$ layer by oil pump vacuum. The light orange liquid was distilled (150 °C, 0.050 mmHg, bulb-to-bulb) to give **1** as a colorless liquid (6.12 g, 5.71 mmol, 75% based upon total alkene). Anal. Calcd for $C_{24}H_{12}F_{39}P$: C, 26.87; H, 1.12. Found: C, 26.71; H, 1.10.

^1H NMR (δ, $CF_3C_6F_{11}$) 1.67 (m, 6H), 2.15 (m, 6H); $^{13}C\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$, partial) 16.5 (d, $^1J_{PC}$ = 16 Hz), 27.6 (dt, $^2J_{PC}$ = 20 Hz, $^2J_{CF}$ = 23 Hz); $^{31}P\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$) −25.5 (s). MS (EI, direct inlet probe, *m*/*z* >724) 1072 (M^+, 100), 1053 ($M^+ - F$, 70), 1003 ($M^+ - CF_3$, 2), 953 ($M^+ - CF_2CF_3$, 2), 903 ($M^+ - (CF_2)_2CF_3$, 5), 853 ($M^+ - (CF_2)_3CF_3$, 4), 803 ($M^+ - (CF_2)_4CF_3$, 2), 753 ($M^+ - (CF_2)_5CF_3$, 1), 739 ($M^+ - CH_2(CF_2)_5CF_3$, 15), 725 ($M^+ - (CH_2)_2(CF_2)_5CF_3$, 2).

$P(CH_2CH_2(CF_2)_7CF_3)_3$ (2). A bomb was charged with $H_2C{=}CH(CF_2)_7CF_3$ (10.02 g, 22.46 mmol), AIBN (0.270 g, 1.64 mmol, 7 mol %), and PH_3 (75 psi, ca. 5.9 mmol)[14,29] in a procedure analogous to that for **1**. After 16 h, the bomb was vented, purged, opened, and analyzed by ^{31}P NMR[16c] as before. Then $CF_3C_6H_5$ (20 mL), VAZO (0.225 g, 0.921 mmol), and $H_2C{=}CH(CF_2)_7CF_3$ (1.00 g, 2.24 mmol) were added. The slightly yellow mixture was kept in a Schlenk flask at 90 °C for 24 h. The solvent was removed by oil pump vacuum to give a white solid. Then $CF_3C_6F_{11}$ (20 mL) and toluene (20 mL) were added. The layers were separated. Volatiles were removed from the $CF_3C_6F_{11}$ layer by oil pump vacuum. The light yellow solid was dissolved in $CF_3C_6H_5$ (ca. 50 mL) and toluene (ca. 40 mL) was added. The sample was cooled to −20 °C. A tan solid precipitated, which was collected by filtration, distilled (175 °C, 5×10^{-5} mmHg, bulb-to-bulb), and dissolved in $CF_3C_6H_5$ (10 mL). The solution was filtered through a silica gel column (2 × 10 cm), which was rinsed with $CF_3C_6H_5$ (100 mL). The solvent was removed by oil pump vacuum to give **2** as a white solid (7.88 g, 5.74 mmol, 70% based upon total alkene), mp 47−48 °C (capillary), 47.5 °C (DSC).[30] Anal. Calcd for $C_{30}H_{12}F_{51}P$: C, 26.25; H, 0.88. Found: C, 26.28; H, 0.93.

^1H NMR (δ, $CF_3C_6F_{11}$) 1.67 (m, 6H), 2.16 (m, 6H); $^{13}C\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$, partial) 16.5 (d, $^1J_{PC}$ = 17 Hz), 27.6 (dt, $^2J_{PC}$ = 21 Hz, $^2J_{CF}$ = 24 Hz); $^{31}P\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$) −25.4 (s). MS (EI, direct inlet probe, *m*/*z* >924) 1372 (M^+, 100), 1353 ($M^+ - F$, 70), 1303 ($M^+ - CF_3$, 2), 1253 ($M^+ - CF_2CF_3$, 3), 1203 ($M^+ - (CF_2)_2CF_3$, 5), 1153 ($M^+ - (CF_2)_3CF_3$, 3), 1103 ($M^+ - (CF_2)_4CF_3$, 2), 1053 ($M^+ - (CF_2)_5CF_3$, 1), 1003 ($M^+ - (CF_2)_6CF_3$, 4), 953 ($M^+ - (CF_2)_7CF_3$, 6), 939 ($M^+ - CH_2(CF_2)_7CF_3$, 15), 926 ($M^+ - (CH_2)_2(CF_2)_7CF_3 + H$, 9), 925 ($M^+ - (CH_2)_2(CF_2)_7CF_3$, 1).

$P(CH_2CH_2(CF_2)_9CF_3)_3$ (3). A bomb was charged with $H_2C{=}CH(CF_2)_9CF_3$ (6.04 g, 11.1 mmol), AIBN (0.200 g, 1.22 mmol, 11 mol %), and PH_3 (75 psi, ca. 6.5 mmol)[14,29] in a procedure analogous to that for **1**. After 12 h, the bomb was repressurized to 75 psi (ca 4.0 mmol). After an additional 12 h, the bomb was vented, purged, opened, and analyzed by ^{31}P NMR[16d] as before. Then $CF_3C_6H_5$ (5 mL), VAZO (0.10 g, 0.41 mmol), and $H_2C{=}CH(CF_2)_9CF_3$ (0.262 g, 0.480 mmol) were added. The mixture was kept in a Schlenk flask at 90 °C for 2 h. The solvent was removed by oil pump vacuum and the residue continuously extracted with benzene in a Soxhlet apparatus. After 24 h, **3** was collected from the thimble as a white solid and dried by oil pump vacuum (4.05 g, 2.42 mmol, 63% based upon total alkene), mp 102−103 °C (capillary), 100.8 °C (DSC).[30] Anal. Calcd for $C_{36}H_{12}F_{63}P$: C, 25.84; H, 0.72. Found: C, 25.64; H, 0.78.

^1H NMR (δ, $CF_3C_6F_{11}$) 1.67 (m, 6H), 2.13 (m, 6H); $^{13}C\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$, partial) 16.4 (m), 27.4 (m); $^{31}P\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$) −25.5 (s). MS (EI, direct inlet probe, *m*/*z* >1224) 1672 (M^+, 100), 1653 ($M^+ - F$, 84), 1603 ($M^+ - CF_3$, 2), 1553 ($M^+ - CF_2CF_3$, 4), 1503 ($M^+ - (CF_2)_2CF_3$, 7), 1453 ($M^+ - (CF_2)_3CF_3$, 7), 1403 ($M^+ - (CF_2)_4CF_3$, 7), 1353 ($M^+ - (CF_2)_5CF_3$, 5), 1303 ($M^+ - (CF_2)_6CF_3$, 3), 1253 ($M^+ - (CF_2)_7CF_3$, 2), 1203 ($M^+ - (CF_2)_8CF_3$, 6), 1153 ($M^+ - (CF_2)_9CF_3$, 10), 1139 ($M^+ - CH_2(CF_2)_9CF_3$, 23), 1126 ($M^+ - (CH_2)_2(CF_2)_9CF_3 + H$, 15), 1125 ($M^+ - (CH_2)_2(CF_2)_9CF_3$, 3).

$O{=}P(CH_2CH_2(CF_2)_5CF_3)_3$ (6). A 1 dram vial was charged with **1** (0.773 g, 0.721 mmol), $CF_3C_6H_5$ (2 mL), and aqueous H_2O_2 (0.5 mL, 30% w/w, ca. 4 mmol). The mixture was shaken vigorously (2 min) and allowed to settle (15 min). A ^{31}P NMR spectrum of the lower $CF_3C_6H_5$ layer showed **6** and a byproduct (δ 43.5, 53.1; 98:2). Water (2 mL) was added, and the layers were separated (aerobic workup). The aqueous layer was washed with $CF_3C_6H_5$ (2 mL). The $CF_3C_6H_5$ layers were combined and dried over $MgSO_4$. The solution was concentrated (ca. 0.5 mL) and stored at −20 °C. After 24 h, the resulting white powder was collected by filtration and dried by oil pump vacuum to give **6** (0.689 g, 0.633 mmol, 88%), mp 52−56 °C (capillary), 53.5 °C (DSC).[30] Anal. Calcd for $C_{24}H_{12}F_{39}PO$: C, 26.48; H, 1.11. Found: C, 26.61; H, 1.05.

^1H NMR (δ, $CF_3C_6F_{11}$) 2.13 (m, 6H), 2.45 (m, 6H); $^{13}C\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$, partial) 19.3 (d, $^1J_{PC}$ = 68 Hz), 24.2 (t, $^2J_{CF}$ = 24 Hz, $w_{1/2}$ = 8 Hz, and $^2J_{PC}$ < 4 Hz); $^{31}P\{^1H\}$ NMR (δ, $CF_3C_6F_{11}$) 41.2 (s). MS (FAB, *m*/*z*) 1089 ($M^+ + 1$, 100).

Reduction of 6. A Schlenk flask was charged with **6** (0.452 g, 0.415 mmol), $CF_3C_6H_5$ (5 mL), $HSiCl_3$ (2.30 g, 17.0 mmol), and N_2 gas, sealed, and placed in a 48 °C oil bath. After 4 h, a ^{31}P NMR spectrum showed **6** to be 90% consumed. After an additional 1 h, volatiles were removed by oil pump vacuum, and $CF_3C_6F_{11}$ (5 mL) and toluene (5 mL) were added to the colorless oily residue. The layers were separated. The solvent was removed from the $CF_3C_6F_{11}$ layer by oil pump vacuum to give a colorless oil (0.430 g) that was distilled (100 °C, 8×10^{-5} mmHg, bulb-to-bulb) to give 0.383 g of a colorless liquid. A ^{31}P NMR spectrum showed a mixture of **1** (96%), **6** (1%), $PH(CH_2CH_2R_{f6})_2$ (2%),[16b] and two unidentified species (δ 103.4, 29.2; 1%, 1%). The liquid was dissolved in $CF_3C_6H_5$. The solution was filtered through a silica gel plug (2 × 1 cm), which was rinsed with $CF_3C_6H_5$. The solvent was removed from the filtrate by oil pump vacuum to give **1** as a colorless liquid (0.377 g, 0.352 mmol, 85%, >97% purity by ^{31}P NMR).

$H_2C{=}CHCH_2(CF_2)_7CF_3$ (7).[21] A Schlenk flask was charged with $ICF_2(CF_2)_6CF_3$ (18.722 g, 34.291 mmol), $Bu_3SnCH_2CH{=}CH_2$ (17.0 mL, 54.8 mmol), and CH_2Cl_2 (20 mL). The solution was photolyzed (Rayonet model RMA-400; R.P.R. 2537 Å lamps). After 1 h, CH_2Cl_2 (20 mL) was added (aerobic workup). The biphasic mixture was extracted with $CF_3C_6F_{11}$ (2 × 10 mL). The solvent was removed from the extracts by rotary evaporation and the residue distilled (77−80 °C, 20 mmHg) to give **7** as a colorless liquid (12.825 g, 27.872 mmol, 81%). Anal. Calcd for $C_{11}H_5F_{17}$: C, 28.71; H, 1.10. Found: C, 28.71; H, 1.16.

^1H NMR (δ, $CDCl_3$) 5.81 (ddt, $^3J_{HH}$ = 17, 11, 7 Hz), 5.35 (dm, $^3J_{HH}$ = 11 Hz), 5.33 (dm, $^3J_{HH}$ = 17 Hz), 2.85 (dtm, $^3J_{HH}$ = 7 Hz, $^3J_{HF}$ = 18 Hz); ^{13}C NMR (δ, $CDCl_3$, partial) 125.4 (d,

(29) The approximate initial amount of PH_3 was calculated as follows. The alkene volume (6.90 g ÷ 1.52 g/mL = 4.54 mL in the preparation of **1**) and the stirring bar volume (0.4 mL) were subtracted from the autoclave volume (30 mL), and the difference utilized in the inert gas equation, n = PV/RT (T = 298 K; 75 psi gauge reading = 5.1 atm above ambient pressure, or 6.1 atm total).

(30) For the graphical method used to obtain the melting point, see Cammenga, H. K.; Epple, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1171; *Angew. Chem.* **1995**, *107*, 1284.

$^1J_{CH}$ = 158 Hz), 122.6 (t, $^1J_{CH}$ = 160 Hz), 36.1 (td, $^1J_{CH}$ = 130 Hz, $^2J_{CF}$ = 22 Hz); ^{19}F NMR (δ, $CDCl_3$) −81.5 (t, J_{FF} = 8 Hz, CF_3), −113.8 (pseudopentet, 2F), −122.4 (m, 6F), −123.3 (m, 2F), −123.6 (m, 2F), −126.8 (m, 2F). IR (cm^{-1}, $CHCl_3$) $\nu_{C=C}$ 1649 m.

P(CH$_2$CH$_2$CH$_2$(CF$_2$)$_7$CF$_3$)$_3$ (4). A bomb was charged with **7** (5.021 g, 10.91 mmol), AIBN (0.183 g, 1.14 mmol, 10 mol %), and PH_3 (100 psi; pressure maintained throughout reaction)[14] in a procedure similar to that for **1**. After 4 h, the bomb was vented, purged, opened, and analyzed by ^{31}P NMR[16e] as before. Then VAZO (0.027 g, 0.11 mmol) and **7** (1.020 g, 2.217 mmol) were added. The mixture was stirred at 100 °C for 12 h and dissolved in $CF_3C_6H_5$ (10 mL). The solution was filtered through a silica gel column (2 × 6 cm), which was rinsed with $CF_3C_6H_5$ (60 mL). The filtrate was concentrated by oil pump vacuum (20 mL) and cooled to 10 °C. A white powder formed, which was collected on a frit. The filtrate was concentrated to 10 mL and cooled to 10 °C. A second crop of white powder formed, which was similarly collected, combined with the first, and dried by oil pump vacuum to give **4** (4.544 g, 3.213 mmol, 73% based upon total alkene), mp 71.5−72.5 °C (capillary), 67.1 °C (DSC).[30] Anal. Calcd for $C_{33}H_{18}F_{51}P$: C, 28.02; H, 1.28. Found: C, 28.16; H, 1.31.

^{1}H NMR (δ, $CF_3C_6F_{11}$) 1.46−1.38 (m, 6H), 1.83−1.69 (m, 6H), 2.23−2.03 (m, 6H); ^{13}C NMR (δ, $CF_3C_6F_{11}$, partial) 32.4 (ttd, $^1J_{CH}$ = 131 Hz, $^2J_{CF}$ = 22 Hz, $^3J_{CP}$ = 12 Hz), 27.3 (td, $^1J_{CH}$ = 126 Hz, $^2J_{CP}$ = 15 Hz), 17.1 (td, $^1J_{CH}$ = 129 Hz, $^1J_{CP}$ = 17 Hz); ^{31}P{^{1}H} NMR (δ, $CF_3C_6F_{11}$) −34.8 (s).

CF$_3$SO$_2$OCH$_2$(CF$_2$)$_7$CF$_3$ (8).[22] A round-bottom flask was charged with $HOCH_2(CF_2)_7CF_3$ (22.472 g, 49.927 mmol), pyridine (4.80 mL, 59.3 mmol), and $CHCl_3$ (100 mL) and placed in a 0 °C bath. Then $(CF_3SO_2)_2O$ (10.0 mL, 59.4 mmol) was added dropwise with stirring over 30 min. The bath was removed. After 12 h, solvent was removed by rotary evaporation (aerobic workup). The white residue was dissolved in ether (250 mL). The solution was washed with cold water (100 mL) and dried over $MgSO_4$. The solvent was removed under vacuum (10 mmHg) to give **8** as a white powder (27.103 g, 46.556 mmol, 93%) mp 33.5 °C (DSC).[30] Anal. Calcd for $C_{10}H_2F_{20}O_3S$: C, 20.63; H, 0.35. Found: C, 20.86; H, 0.42.

^{1}H NMR (δ, $CDCl_3$) 4.82 (t, $^3J_{HF}$ = 12 Hz); ^{13}C (δ, $CDCl_3$, partial) 68.3 (tt, $^1J_{CH}$ = 157 Hz, $^2J_{CF}$ = 28 Hz); ^{19}F (δ, $CDCl_3$) −74.5 (t, J_{FF} = 12 Hz, CF_3), −81.3 (m, 2F), −120.2 (m, 2F), −122.3 (m, 6F), −123.3 (m, 2F), −126.6 (m, 2F).

ICH$_2$(CF$_2$)$_7$CF$_3$ (9). A round-bottom flask was charged with **8** (27.103 g, 46.556 mmol), KI (15.495 g, 93.342 mmol), and ethylene glycol (270 mL) and fitted with a condenser. The mixture was refluxed for 12 h and cooled. Water was added (270 mL; aerobic workup). The mixture was extracted with ether (2 × 150 mL). The extracts were washed with aqueous $Na_2S_2O_3$ (100 mL, 0.10 M) and dried over $MgSO_4$. The solvent was removed under vacuum (10 mmHg) to give **9** as a white powder (24.324 g, 43.437 mmol, 93%), mp 37.2 °C (DSC).[30] Anal. Calcd for $C_9H_2F_{17}I$: C, 19.30; H, 0.36. Found: C, 19.28; H, 0.42.

^{1}H NMR (δ, $CDCl_3$) 3.64 (t, $^3J_{HF}$ = 17 Hz); ^{13}C NMR (δ, $CDCl_3$, partial) −4.1 (tt, $^1J_{CH}$ = 151 Hz, $^2J_{CF}$ = 26 Hz); ^{19}F NMR (δ, $CDCl_3$) −81.3 (t, J_{FF} = 12 Hz, CF_3), −107.4 (pseudopentet, 2F), −121.9 (m, 2F), −122.2 (m, 2F), −122.3 (m, 4F), −123.2 (m, 2F), −126.6 (m, 2F).

H$_2$C=CHCH$_2$CH$_2$(CF$_2$)$_7$CF$_3$ (10).[23] A Schlenk flask was charged with **9** (10.075 g, 17.991 mmol), $Bu_3SnCH_2CH{=}CH_2$ (8.40 mL, 27.1 mmol), VAZO (0.4327 g, 1.771 mmol, 10 mol %), and $CF_3C_6H_5$ (50 mL) and fitted with a condenser. The solution was refluxed for 6 h. The solvent was removed by rotary evaporation, and CH_2Cl_2 (100 mL) was added. The biphasic mixture was extracted with $CF_3C_6F_{11}$ (2 × 20 mL). The solvent was removed from the extracts by rotary evaporation. The residue was distilled (74−75 °C, 15 mmHg) to give **10** as an analytically impure colorless liquid (4.783 g, 10.09 mmol, 56%). Anal. Calcd for $C_{12}H_7F_{17}$: C, 30.40; H, 1.49. Found: C, 31.32; H, 1.61.

^{1}H NMR (δ, $CDCl_3$) 5.90−5.76 (m, 1 H), 5.17−5.05 (m, 2 H), 2.42−2.33 (m, 2 H), 2.27−2.07 (m, 2 H); ^{13}C NMR (δ, $CDCl_3$, partial) 135.7 (d, $^1J_{CH}$ = 155 Hz), 116.5 (t, $^1J_{CH}$ = 154 Hz), 30.7 (tt, $^1J_{CH}$ = 129 Hz, $^2J_{CF}$ = 22 Hz), 24.6 (tt, $^1J_{CH}$ = 128 Hz, $^3J_{CF}$ = 4 Hz); ^{19}F NMR (δ, $CDCl_3$) −81.5 (J_{FF} = 9 Hz, CF_3), −115.1 (pseudopentet, 2F), −122.3 (m, 2F), −122.5 (m, 4F), −123.3 (m, 2F), −124.1 (m, 2F), −126.7 (m, 2F). IR (cm^{-1}, neat) $\nu_{C=C}$ 1647 m.

P(CH$_2$CH$_2$CH$_2$CH$_2$(CF$_2$)$_7$CF$_3$)$_3$ (5). A bomb was charged with **10** (5.017 g, 10.58 mmol), AIBN (0.175 g, 1.06 mmol, 10 mol %), and PH_3 (100 psi)[14] in a procedure analogous to that for **4**. After 4 h, the bomb was vented, purged, opened, and analyzed by ^{31}P NMR[16a,f] as before. Then VAZO (0.209 g, 0.855 mmol) and **10** (0.781 g, 1.65 mmol) were added. The mixture was stirred at 100 °C for 12 h and dissolved in $CF_3C_6H_5$ (10 mL). The solution was filtered through a silica gel column (2 × 6 cm), which was rinsed with $CF_3C_6H_5$ (60 mL). The solvent was removed from the filtrate by oil pump vacuum. The residue was dissolved in toluene (50 mL), and the solution was cooled to 10 °C. A white powder formed, which was collected on a frit. The filtrate was concentrated to 10 mL and cooled to 10 °C. A second crop of white powder formed, which was similarly collected, combined with the first, and dried by oil pump vacuum to give **5** (3.905 g, 2.681 mmol, 66% based upon total alkene), mp 44.5−45.0 °C (capillary), 40.2 °C (DSC).[30] Anal. Calcd for $C_{36}H_{24}F_{51}P$: C, 29.69; H, 1.66. Found: C, 29.52; H, 1.66.

^{1}H NMR (δ, $CF_3C_6F_{11}$) 2.08−1.96 (m, 6H), 1.74−1.69 (m, 6H), 1.55−1.45 (m, 6H), 1.39−1.33 (m, 6H); ^{13}C NMR (δ, $CF_3C_6F_{11}$, partial) 30.9 (tt, $^1J_{CH}$ = 129 Hz, $^2J_{CF}$ = 22 Hz), 27.7, 25.9 (2 × td, $^1J_{CH}$ = 125/125 Hz, $^2J_{CP}$ = 15/16 Hz), 21.9 (td, $^1J_{CH}$ = 129 Hz, $^1J_{CP}$ = 11 Hz); ^{31}P{^{1}H} NMR (δ, $CF_3C_6F_{11}$) −32.8 (s).

Partition Coefficients. The following procedure is representative. A 1 dram vial was charged with **1** (0.0390 g, 0.0364 mmol), $CF_3C_6F_{11}$ (2.000 ± 0.015 mL), and toluene (2.000 ± 0.015 mL), capped with a mininert valve, vigorously shaken (2 min), and immersed (cap-level) in a 35 °C bath. After 12 h, the bath was removed. After 1 h (ambient temperature 24 °C), the vial was taken into a drybox (27 °C). After 1 h, 0.400 ± 0.005 mL aliquots of each layer were added to stock solutions of hexadecane in hexane (2.000 ± 0.015 mL, 0.00222 M; for **4** and **5**, 0.0111 M eicosane in hexanes). GLC analysis showed 8.52×10^{-5} mmol and 7.11×10^{-3} mmol of **1** in the toluene and $CF_3C_6F_{11}$ aliquots, for a 98.8(0.5):1.2(0.5) ratio (Table 1; 3−11 injections averaged for each run). The total amount of **1** calculated from these data (0.0386 g or 0.0360 mmol using a 2.000/0.400 volume multiplier) is in close agreement with that utilized.

Acknowledgment. We thank the NSF (CHE-9401572) for support of this research, Mr. Lazslo Kiss for some exploratory reactions, Professor A. Rheingold (University of Delaware) for preliminary X-ray data, and Dr. István Horváth (Exxon Corporate Research) for many helpful discussions.

Supporting Information Available: Instrumental data and NMR spectra with resonance assignments (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980692Y