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Novel Perfluoroalkyl-Diphenylphosphine Compounds. Syntheses and Reaction Mechanisms

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A new class of perfluoroalkyl compounds, containing novel R_f-Ph_2P bonds (where R_f is the perfluoroalkyl moiety), were synthesized in fairly good yields, and their reaction mechanisms were studied in different solvents. Thus, the reaction of 1-iodo-*n*-perfluorohexane (**1a**) in liquid ammonia afforded only the hydro deiodination product (**3a**), and under irradiation a low yield of diphenyltridecafluorohexylphosphine (**2a**) was obtained. However, good yields (≥72%) of substitution products were obtained with **1a** and 1-iodo-*n*-perfluorobutane (**1c**) under irradiation in HMPA and DMPU as solvents. These reactions were completely inhibited with di-*tert*-butyl nitroxide, a good free radical scavenger. The photostimulated reaction of 1,4-diiodoperfluorobutane (**1d**) in HMPA afforded the disubstitution product in 55% isolated yield. Low yields of substitution products were obtained with **1a** and **1c** either in the dark or under irradiation in tetraglyme. It is suggested that the reactions in HMPA and DMPU occur by the $S_{RN}1$ mechanism, whereas halogen metal exchange is the main reaction in liquid ammonia and tetraglyme.

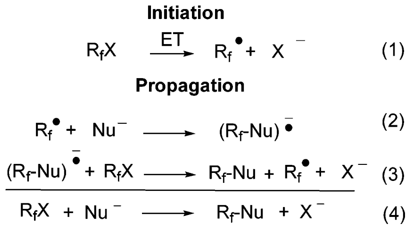
Introduction

Perfluoroalkyl compounds have attracted much attention during the past twenty years for their notorious applications in different fields of chemistry. The syntheses of these compounds cannot be achieved through classical nucleophilic substitutions on perfluoroalkyl halides, R_fX, as these substrates are impeded to react by the S_N1 mechanism, on account of the low stability of carbocations, and precluded to undergo S_N2 substitutions, due to repulsion of the lone electron pairs of the fluorine atoms to the backside attack by the nucleophile.

Compounds bearing the perfluoroalkyl moiety (R_f)−C bond have been synthesized by different routes. One such synthetic path involves addition of $R_f^\bullet$ radicals to double bonds.[1]

Different R_f−heteroatom bonds have been attained with other group XIV elements, i.e., R_f-Si,[2] R_f-Ge,[3] and R_f-Sn[4] bonds. Compounds with perfluoroalkyl moieties bonded to group XV elements are less ubiquitous, and their occurrence is mainly represented by R_f-N.[4,5] Perfluoroalkylarsines[6] and perfluoroalkylstibines have rarely been cited in the literature.[7] To the best of our knowledge there is only one report on the synthesis of a tris(perfluoroalkyl)phosphine. This compound is obtained via a direct elemental fluorination of trialkylphosphines.[8] Diphenylperfluoroalkoxy phosphines have recently been prepared and used as ligands in selective hydrogenation through rhodium catalysis.[9]

Scheme 1



Another route to the synthesis of compounds with perfluoroalkyl moieties is through the $S_{RN}1$ mechanism, which involves radicals and radical ions as intermediates.[10] The $S_{RN}1$ mechanism is a chain process and is presented in Scheme 1. In the initiation step, the radical of the substrate is formed by an ET from the nucleophile

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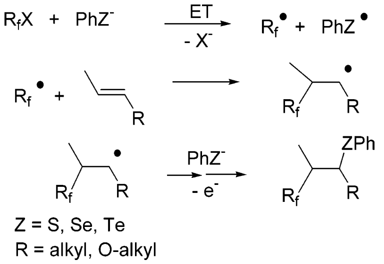
Scheme 2



or from a suitable electron source (eq 1). The ET to unsubstituted alkyl halides is proposed to be dissociative.[11]

The $R_f^\bullet$ radical reacts with the nucleophile to give the radical anion of the substitution product (eq 2), which by ET to the substrate (eq 3), forms the intermediates needed to continue the propagation cycle. This whole process affords a nucleophilic substitution (eq 4). The mechanism has termination steps that depend on the substrate, nucleophile, solvent, and experimental conditions.

Inhibition by radical traps has been extensively used to provide mechanistic evidence. The most commonly employed are di-*tert*-butylnitroxide (DTBN) and radical anion scavengers such as *p*-dinitrobenzene (*p*-DNB).[10]

Among group XVI elements, compounds bearing R_f-O, R_f-S, and R_f-Se bonds have been reported, their route of syntheses being mainly by the $S_{RN}1$ mechanism.[12]

The reaction of R_fX with PhZ^- (Z = S, Se, Te) in the presence of olefins has been shown to be a route to the synthesis of α,β-perfluoroalkylphenylchalcogenides.[13] The $R_f^\bullet$ radicals generated by ET from PhZ^- to R_fI add the olefin to afford a new radical, which after coupling with PhZ^- affords the intermediates that continue a $S_{RN}1$-like propagation cycle (Scheme 2). A similar behavior has been observed with the alkyne derivatives.[14]

We wish to report herein a straightforward and facile approach to the synthesis of perfluoroalkyl diphenylphosphines, Ph_2P-R_f, which involves the reaction of diphenylphosphide anion (Ph_2P^-) on perfluoroalkyliodides R_fI, in solvents such as liquid ammonia, hexamethylphosphoramide (HMPA), *N*,*N*-dimethylpropyleneurea (DMPU), and tetraethylene glycol dimethyl ether (tetraglyme).

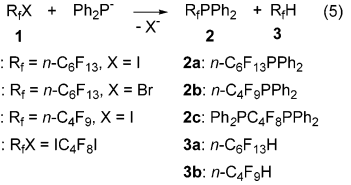
Table 1. Reactions of R_fX with Ph_2P^- Ions in HMPA

expt	R_fX	reaction conditions[a]	products (yield %)[b]
1	n-$C_6F_{13}I$[c]	dark[d]	n-$C_6F_{13}I$ (30), n-$C_6F_{13}PPh_2$ (0); n-$C_6F_{13}H$ (55)
2	n-$C_6F_{13}I$[c]	$h\nu$[d]	n-$C_6F_{13}I$ (15), n-$C_6F_{13}PPh_2$ (20); n-$C_6F_{13}H$ (60)
3	n-$C_6F_{13}I$[c]	dark	n-$C_6F_{13}PPh_2$ (56)[e]
4	n-$C_6F_{13}I$[c]	$h\nu$	n-$C_6F_{13}PPh_2$ (85)[e]
5	n-$C_6F_{13}I$[c]	$h\nu$, *p*-DNB[f]	n-$C_6F_{13}PPh_2$ (79)[e]
6	n-$C_6F_{13}I$[c]	$h\nu$, DTBN[f]	n-$C_6F_{13}PPh_2$ (0)[e]
7	n-$C_6F_{13}Br$[c]	$h\nu$	n-$C_6F_{13}PPh_2$ (15)[e]
8	n-C_4F_9I[g]	dark	n-$C_4F_9PPh_2$ (36)[e]
9	n-C_4F_9I[g]	dark (66 h)	n-$C_4F_9PPh_2$ (60)[e]
10	n-C_4F_9I[g]	dark, *p*-DNB[f]	n-$C_4F_9PPh_2$ (30)[e]
11	n-C_4F_9I[g]	$h\nu$	n-$C_4F_9PPh_2$ (65)[e]
12	n-C_4F_9I[g]	$h\nu$[h]	n-$C_4F_9PPh_2$ (72)[e]
13	n-C_4F_9I[g]	$h\nu$, *p*-DNB[f]	n-$C_4F_9PPh_2$ (60)[e]
14	n-C_4F_9I[g]	$h\nu$, DTBN[f]	n-$C_4F_9PPh_2$ (0)[e]
15	IC_4F_8I[i]	$h\nu$	$Ph_2PC_4F_9PPh_2$ (55)[j]

[a] The concentration of Ph_2P^- was 2.3×10^{-2} M, reaction time 2 h, unless otherwise indicated. [b] Product yields were determined by GC analyses, employing the internal standard method and calibrated with the response of an authentic sample. [c] **1a** was 5.3×10^{-2} M. Product yields were based on starting PPh_3 concentration. [d] The solvent was liquid ammonia (250 mL), and the concentration of Ph_2P^- ions was 1.2×10^{-3} M and of **1a** was 2.8×10^{-3} M. [e] The overall mass balance is ca. 95% in all cases. Unreacted **1** accounted for the remainder of the yields with **3** in less than 5%. [f] In 15 mol %. [g] **1c** was 1.2×10^{-2} M. Product yields were based on starting **1c**. [h] After 2 h of irradiation the reaction mixture was keep 22 h in the dark. [i] **1d** was 1.2×10^{-2} M. Product yields were based on starting **1d**. [j] Isolated yield.

Results and Discussion

The Ph_2P^- anion is readily formed in liquid ammonia from Ph_3P and sodium metal and under photostimulation reacts with different substrates by the $S_{RN}1$ mechanism.[10] We allowed this ion to react with R_fX in liquid ammonia under different experimental conditions, according to a general scheme shown in eq 5.



$$\underset{\mathbf{1}}{R_fX} + Ph_2P^- \xrightarrow[-X^-]{} \underset{\mathbf{2}}{R_fPPh_2} + \underset{\mathbf{3}}{R_fH} \qquad (5)$$

1a: R_f = n-C_6F_{13}, X = I
1b: R_f = n-C_6F_{13}, X = Br
1c: R_f = n-C_4F_9, X = I
1d: R_fX = IC_4F_8I
2a: n-$C_6F_{13}PPh_2$
2b: n-$C_4F_9PPh_2$
2c: $Ph_2PC_4F_8PPh_2$
3a: n-$C_6F_{13}H$
3b: n-C_4F_9H

When compound **1a** is subjected to reaction (2 h) with Ph_2P^- ions in liquid ammonia in the dark, only the reduced product **3a** is formed along with unreacted **1a**. Upon irradiation, compound **2a** is obtained in low yields (expts 1 and 2, Table 1).

Compound **2a** was isolated by reduced-pressure distillation from the evaporated extracts, was characterized by standard spectroscopic techniques, and remained stable (unoxidized) for prolonged periods of time (more than a month, at room temperature). If, instead, the crude reaction mixtures were subjected to silica gel chromatography, an oxidized product was recovered. Compound **2a** was also oxidized in the workup procedure by treatment with 10% hydrogen peroxide, and the purified product was identified as *n*-perfluorohexyldiphenylphosphine oxide. As the reaction is accelerated by light, an $S_{RN}1$ component is advised.

Although the total conversion was 80%, the product yields were low, due to the presence of reduced products

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3a. This reduced product **3a** probably arises through a halogen−metal exchange (HME) reaction.

We had previously reported that the generation of trimethylsilyl and trimethylstannyl ions proceeds quite well in HMPA as solvent.[15] We generated Ph_2P^- ions in HMPA, by allowing PPh_3 to react with sodium metal under ultrasound conditions. This method of generating the anion (which develops an intense red color in HMPA) provided a high-yield source (>90%) of Ph_2P^- ions, as determined by a nucleophilic reaction with benzyl chloride to yield benzyl-diphenyl-phosphine.

Upon 2 h reaction of Ph_2P^- ions with substrates **1a** and **1c** (eq 5), the substitution products **2a** and **2b** were found (56% and 36% yields, respectively, expts 3 and 8, Table 1), together with unreacted **1a** and **1c** and small amounts of **3a** and **3b**. Substrate **1c** afforded 60% yield of substitution product **2b** on prolonged reaction times (66 h) (Table 1, expt 9).

These reactions are accelerated by light. Thus **1a** and **1c** furnished **2a** and **2b** (in 85% and 65% yields, respectively) after 2 h of irradiation. Global product yield for **2b** was maximized upon 2 h irradiation of **1c** in the presence of Ph_2P^- ions and allowing the mixture to react further in the dark (22 h). Thus the yield of **2b** was increased up to 72% (expts 4, 11, and 12, Table 1).

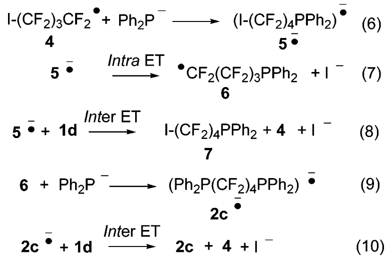
These reactions are not inhibited by *p*-DNB (expts 5, 10, and 13, Table 1), but quenched completely by DTBN, a good radical scavenger (expts 6 and 14, Table 1). Different experimental conditions were attempted in this solvent, to maximize the product yields, and the best results are reported in expt 4, Table 1.

When substrate **1b** is subjected to a photostimulated reaction with Ph_2P^- anion, lower yields of substitution product **2a** are found (15% yield, expt 7, Table 1). This is consistent with the tenet that bromine is a worse leaving group than iodine in $S_{RN}1$ reactions.

The fact that the reactions in HMPA are accelerated by light, and suppressed entirely by a radical scavenger such as DTBN, is indicative of the intermediacy of an $S_{RN}1$ process. That these reactions have an important spontaneous component (the dark reactions proceed in fairly good yields) could suggest that there is an in-cage thermally spontaneous ET process given the good electron acceptor nature of the substrates and electron donor capability of the nucleophile.

The photostimulated reaction in 2 h of 1,4-diiodoperfluorobutane (**1d**) yields the disubstitution product **2c** in 55% isolated yield (expt 15, Table 1). Once radical **4** is formed in the initiation step, it couples with Ph_2P^- ions to yield the radical anion intermediate $\mathbf{5}^{-\bullet}$ (eq 6). This radical anion is prone to undergoing two competing reactions: intramolecular ET to give the radical **6** (eq 7) and intermolecular ET to **1d** to afford the monosubstitution product (4-iodoperfluorobutyl)diphenylphosphine **7** and **4** (eq 8). The fact that **7** was not formed in these reactions is indicative that the intramolecular ET of the radical anion intermediate $\mathbf{5}^{-\bullet}$ to form the radical **6** is faster than the intermolecular ET to **1d** (Scheme 3). Radical **6** couples with the nucleophile to afford ultimately the disubstitution product **2c** (eqs 9 and 10).

Scheme 3



$$I\text{-}(CF_2)_3CF_2^{\bullet} + Ph_2P^- \longrightarrow (I\text{-}(CF_2)_4PPh_2)^{\bar{\bullet}} \quad (6)$$

$$\mathbf{5}^{\bar{\bullet}} \xrightarrow{\textit{Intra}\ \mathrm{ET}} {}^{\bullet}CF_2(CF_2)_3PPh_2 + I^- \quad (7)$$

$$\mathbf{5}^{\bar{\bullet}} + \mathbf{1d} \xrightarrow{\textit{Inter}\ \mathrm{ET}} I\text{-}(CF_2)_4PPh_2 + \mathbf{4} + I^- \quad (8)$$

$$\mathbf{6} + Ph_2P^- \longrightarrow (Ph_2P(CF_2)_4PPh_2)^{\bar{\bullet}} \quad (9)$$

$$\mathbf{2c}^{\bar{\bullet}} + \mathbf{1d} \xrightarrow{\textit{Inter}\ \mathrm{ET}} \mathbf{2c} + \mathbf{4} + I^- \quad (10)$$

Table 2. Reactions of R_fI with Ph_2P^- Ions in DMPU and Tetraglyme

expt	R_fX	reaction conditions[a]	products (%)[b]
1	n-$C_6F_{13}I$	dark, DMPU	n-$C_6F_{13}PPh_2$ (55), n-$C_6F_{13}H$ (30)
2	n-$C_6F_{13}I$	*hν*, DMPU	n-$C_6F_{13}PPh_2$ (78), $C_6F_{13}H$ (10)
3	n-$C_6F_{13}I$	dark, TG	n-$C_6F_{13}PPh_2$ (19), $C_6F_{13}H$ (45)
4	n-$C_6F_{13}I$	*hν*, TG	n-$C_6F_{13}PPh_2$ (20), $C_6F_{13}H$ (41)
5	n-$C_6F_{13}I$	*hν*, *p*-DNB,[c] TG	n-$C_6F_{13}PPh_2$ (21), $C_6F_{13}H$ (45)
6	n-$C_6F_{13}I$	*hν*, DTBN,[c] TG,	n-$C_6F_{13}PPh_2$ (20), $C_6F_{13}H$ (39)
7	n-C_4F_9I	dark, DMPU	n-$C_4F_9PPh_2$ (43), n-C_4F_9H (30)
8	n-C_4F_9I	*hν*, DMPU	n-$C_4F_9PPh_2$ (68), n-C_4F_9H (22)
9	n-C_4F_9I	*hν*, DTBN,[c] DMPU	n-$C_4F_9PPh_2$ (0), n-C_4F_9H (43)
10	n-C_4F_9I	dark, TG	n-$C_4F_9PPh_2$ (35), n-C_4F_9H (22)
11	n-C_4F_9I	*hν*, TG	n-$C_4F_9PPh_2$ (31), n-C_4F_9H (27)

[a] Reactions were carried out in 2 h with 2.3×10^{-2} M (DMPU) and 1.3×10^{-2} M (tetraglyme, TG) of Ph_2P^- ions. **1** was 6.9×10^{-2} M. Product yields were based on starting PPh_3 concentration. [b] Product yields were determined by GC analyses, employing the internal standard method and calibrated with the response of an authentic sample (n-$C_6F_{13}PPh_2$ or n-$C_4F_9PPh_2$). Yields of reduced products $C_6F_{13}H$ and n-C_4F_9H were determined by GC, using an internal standard method and assuming response factors equal to those of the substrates. Unreactive stating material accounted for the rest of the yield. The overall mass balance is ca. 95% in all cases. [c] 15% molar weight of DTBN.

To avoid the inherent toxicity related to the use of HMPA solutions, we undertook the nucleophilic substitution reactions of R_fI with PPh_2^- ions in DMPU[16−18] as solvent. The Ph_2P^- ion was generated by allowing PPh_3 and sodium metal to react under ultrasound conditions. Compounds **2a** and **2b** are obtained under dark reaction conditions, but upon irradiation the products are obtained in higher yields (78% and 68% yields, respectively, expts 1, 2, 7, and 8, Table 2). The photostimulated reaction of **1c** was completely inhibited by DTBN (expt 9, Table 2). An $S_{RN}1$ mechanism also accounts for these observations.

Generation of Ph_2P^- ions in tetraglyme proceeds smoothly at room temperature under ultrasound conditions, through reaction of sodium metal and Ph_3P. We trapped Ph_2P^- ions (which give a deep red-colored solution in this solvent) through reaction with benzyl chloride, which rendered over 80% of substitution product benzyldiphenylphosphine. Upon reaction of Ph_2P^- ions with substrates **1a** and **1c**, substitution products **2a** and **2b** were obtained, albeit in rather poor yields (ca. 20%) according to the conditions reported in Table 2 (expts 3 and 10). In the reaction mixture, high

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amounts of reduction products **3a** and **3b** prevail. The reaction seems not to be accelerated by light nor inhibited by *p*-DNB or DTBN (expts 4–6, 10, and 11, Table 2). This would seem to be indicative of the absence of free radicals and radical anions in tetraglyme solutions.

Summary and Conclusions

We have found a versatile and high-yield method for the synthesis of novel R_f-PPh_2 compounds upon reaction of Ph_2P^- ions and R_fI in highly coordinating solvents such as HMPA and DMPU. With substrates bearing two living groups, such as **1d**, the disubstitution product is obtained in good yield. It can be concluded that reactions carried out in HMPA or DMPU occur by the $S_{RN}1$ mechanism, whereas those in liquid ammonia and tetraglyme are mainly HME reactions.

Experimental Section

General Methods. The internal standard method was used for quantitative GC analysis using authentic samples, and one of the following capillary columns was employed: HP-1 (5 m × 0.53 mm i.d.) or HP-1 (30m × 0.32 mm i.d.). ^{1}H NMR (200.13 and 400.23 MHz) and ^{13}C NMR (50.32 and 100.64 MHz) analyses were conducted in deuteriochloroform (or otherwise indicated) as solvent and referenced with the residual solvent peak. ^{31}P NMR spectra of phosphine oxides were performed on a Bruker AM 500 sprectrometer (202.46 MHz) using diethyl phosphite as external standard. Chemical shifts are in δ units downfield from the external standard. GC/MS analyses were carried out on a Shimadzu QP-5050 chromatograph coupled with a mass selective detector and a DB-5 (30 m × 0.25 mm i.d.) capillary column. High-resolution mass spectrometry measurements were done at the Mass Spectrometry Facility, Faculty of Medicine, University of Toronto.

Materials. HMPA, DMPU, and tetraglyme were double-distilled and stored over molecular sieves (4 Å). Substrates **1a**–**d** were commercially available and used as received from the supplier.

Reactions in HMPA, DMPU, and Tetraglyme: General Procedure. Into a 10 mL glass tube sealed with a rubber septum, which was previously flame-dried under vacuo, 2 mL of solvent was added. The solvent was heated under vacuum and left to stand to reach room temperature, and sodium metal was then added. After this addition, the tube was deoxygenated and refilled with a N_2 atmosphere three times. The tube was immersed in an ultrasound bath and sonicated for 2 h, to allow sodium to dissolve. A deep blue solution is obtained (brown in DMPU and blue in tetraglyme). At this point, PPh_3 in 1 mL of previously deoxygenated solvent was added through a syringe. The mixture was again immersed in an ultrasound bath and sonicated for 2 h. The reaction mixture turned deep red, indicating the formation of Ph_2P^- ions. The solution was transferred through a cannula to another previously flame-dried 10 mL tube equipped with a stir bar, under N_2 atmosphere, through a rubber septum and positive N_2 pressure. Thisprevents undissolved sodium from remaining in the reaction medium. The stirring was started, and substrate **1a**, **1b**, or **1c** was added as a neat compound through a microliter syringe. For the dark arm of the reactions, the tubes were covered in aluminum foil to protect them from laboratory light. For the photochemical counterpart, the tubes were irradiated either in a photochemical reactor using two medium-pressure water-cooled Hg lamps emitting maximally at 366 nm or in an air-cooled Rayonet reactor charged with 12 3500 Å lamps.

The experiments in HMPA were conducted with ca. 2.3×10^{-2} M of Ph_2P^- ions, and the reaction times elapsed for 2 h. The concentration of **1a** was 5.3×10^{-2}, and that of **1c** and **1d** 1.2×10^{-2} M. In DMPU the experiments were conducted with ca. 2.3×10^{-2} M of Ph_2P^- ions and 6.9×10^{-2} M **1a** and **1c**. In tetraglyme the experiments were conducted with 1.3×10^{-2} M of Ph_2P^- ions and 3.8×10^{-2} M **1a** and **1c**.

The workup consisted in pouring distilled water into the reaction tubes, neutralizing with ammonium nitrate solution, and extracting the aqueous phase with hexane three times. The hexane layers were dried over anhydrous sodium sulfate and filtered, an internal standard (triphenylstibine) was added, and the mixture was made up to volume and analyzed by GC and GC/MS to check for volatile material (i.e., reduced products **3a** and **3b**). The solvent (hexane) was then distilled carefully under atmospheric pressure, and the residue was redistilled under reduced pressure using a Kügelrohr apparatus. The volatile fractions contained traces of Ph_3P (and standard), and the higher boiling point fraction was collected. For the reactions in HMPA the substitution compounds **2a** (98% purity; ≥75% isolated yield, 85% GC yield, expt 4, Table 1) and **2b** (95% purity, 51% isolated yield, 65% GC yield, expt 11, Table 1) were obtained. The materials were pure enough for spectroscopic characterization.

Reactions in Liquid Ammonia. Into a three-necked round-bottomed flask equipped with a coldfinger condenser charged with ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 250 mL of ammonia previously dried with sodium metal under nitrogen. To the ammonia, sodium metal (1.3×10^{-2} mol, 0.290 g) and PPh_3 (5.8×10^{-3} mol, 1.506 g) were added, waiting for the formation of Ph_2P^- to occur (20 min), indicated by a deep orange solution. The substrate **1a** was then added by weighed microliter syringe (1.7×10^{-2} mol) and the solution irradiated in a photochemical reactor using two medium-pressure water-cooled Hg lamps emitting maximally at 366 nm for 2 h. For quantitative purposes, an adequate internal standard was added previous to ammonia evaporation. The workup was the same as that indicated for the reactions in HMPA.

Products. 2a ($Ph_2PC_6F_{13}$): colorless oil. GC/MS EI, *m*/*z* (%): 504 (14), 186 (12), 185 (100), 183 (68), 152 (8), 107 (6), 92 (12), 69 (7). EI-HRMS Anal. Calcd for $C_{18}H_{10}F_{13}P$: 504.0316. Found: 504.0321. ^{1}H NMR δ_H ppm (200.13 MHz, $CDCl_3$): 7.76–7.64 (4 H, br m); 7.48–7.28 (6 H, br m). ^{13}C NMR $\delta_{^{13}C}$ (50.32 MHz, $CDCl_3$): 128.71 (d, $^2J_{P-C} = 9.5$ Hz); 130.90; 135.25 (d, $^1J_{P-C} = 23.1$ Hz).

Perfluorohexyldiphenylphosphine oxide ($Ph_2P(O)$-C_6F_{13}): yellowish oil. GC/MS EI, *m*/*z* (%): 520 (4), 202 (12), 201 (100), 77 (28), 51 (12). EI-HRMS Anal. Calcd for $C_{18}H_{10}F_{13}OP$: 520.0262. Found: 520.0213. ^{1}H NMR δ_H ppm (400.23 MHz, $CDCl_3$): 7.68–7.52 (cplx m, 3 H), 7.43–7.29 (cplx m, 5 H), 7.26–7.00 (cplx m, 2 H). ^{13}C NMR $\delta_{^{13}C}$ (100.24 MHZ, CD_3OD): 130.56 ($^1J_{P-C} = 12.2$ Hz); 133.71 ($^2J_{P-C} = 9.6$ Hz); 135.85 ($^3J_{P-C} = 2.7$ Hz). ^{31}P NMR ($CDCl_3$, 202.46 MHz): $\delta_{^{31}P}$ ppm: 24.59 (t, $^2J(^{31}P-^{19}F) = 7.1$ Hz).

2b ($Ph_2PC_4F_9$): colorless oil. GC/MS EI, *m*/*z* (%): 404 (15), 185 (95), 183 (100), 152 (13), 107 (12), 91 (18), 69 (8), 51 (9). EI-HRMS Anal. Calcd for $C_{16}H_{10}F_9P$: 404.0376. Found: 404.0379. ^{1}H NMR $\delta_{^1H}$ ppm (400.23 MHz, $CDCl_3$): 7.10–7.55 (cplx m, 3H); 7.61–8.14 (cplx m, 7H). ^{13}C NMR $\delta_{^{13}C}$ (100.24 MHZ, CD_3OD): 129.61 ($^2J_{P-C} = 9.6$ Hz); 130.04; 134.71 ($^1J_{P-C} = 23.1$ Hz).

Perfluorobutylldiphenylphosphine oxide ($Ph_2P(O)$-C_4F_9): yellowish oil. GC/MS EI, *m*/*z* (%): 201 (15), 171 (8), 77 (35), 69 (12), 51 (30), 152 (8). EI-HRMS (for *m*/*z* 420, 3%) Anal. Calcd for $C_{16}H_{10}F_9OP$: 420.0326. Found: 420.0327. ^{1}H NMR $\delta_{^1H}$ (400.23 MHz, $CDCl_3$): 7.22–7.43 (cplx m, 3H); 7.60–7.75 (cplx m, 7H). ^{13}C NMR $\delta_{^{13}C}$ (125 MHz $CDCL_3$): 125.70 ($^1J_{P-C}$ 105.9 Hz), 128.05 ($^2J_{P-C}$ 12.6 Hz), 132.35 ($^3J_{P-C}$ 1.8 Hz), 133.8. ^{31}P NMR ($CDCl_3$, 202.46 MHz): $\delta_{^{31}P}$ 24.41 (t, $^2J(^{31}P-^{19}F) = 7.1$ Hz).

1,4-Bis(diphenylphosphanyl)perfluorobutane (Ph_2-$PC_4F_8PPh_2$, 2c): yellowish oil. GC/MS EI, *m*/*z* (%): 570 (6), 493 (7), 413 (100), 385 (67), 184 (25). EI-HRMS (for *m*/*z* 570, 6%) Anal. Calcd for $C_{28}H_{20}F_8P_2$: 570.0913. Found: 570.0934. ^{1}H NMR $\delta_{^1H}$ (400.23 MHz, $CDCl_3$): 6.85−7.17 (cplx m, 4H); 7.41−7.71 (cplx m, 6H).

1,4-Bis(diphenylphosphinoyl)perfluorobutane ($Ph_2P(0)C_4F_8P(0)Ph_2$): ^{31}P NMR ($CDCl_3$, 202.46 MHz) $\delta_{^{31}P}$ 24.42 (t, $^2J(^{31}P-^{19}F) = 7.1$ Hz).

3a ($C_6F_{13}H$):[17] GC/MS EI *m*/*z* (%) 131 (100), 170 (75), 101 (68), 169 (36), 151 (35), 117 (30), 181 (20), 201 (10), 231 (10), 431 (8).

3b (C_4F_9H):[18] GC/MS EI *m*/*z* (%) 131 (100), 119 (63), 169 (55), 129 (50), 100 (40), 181 (18), 219 (18), 419 (10), 331 (8).

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of compounds **2a** and **2b**. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of perfluorohexyldiphenylphosphine oxide and perfluorobutyldiphenylphosphine oxide. ^{1}H NMR spectra of compounds **2c** and ^{31}P NMR of 1,4-bis(diphenylphosphinoyl)perfluorobutane ($Ph_2P(0)C_4F_8P(0)Ph_2$). This material is available free of charge via the Internet at http://pubs.acs.org.

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