Synthetic Methods

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Synthesis and Properties of Perfluoroalkyl Phosphine Ligands: Photoinduced Reaction of Diphosphines with Perfluoroalkyl Iodides**

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Organophosphorus compounds are widely used as ligands in metal catalysts. Specifically, perfluoroalkylated phosphines are gaining attention because of their fluorous affinity.[1] In 1994, Horváth and co-workers reported that rhodium complexes with perfluoroalkylated phosphine ligands, which were employed in the hydroformylation of alkenes, could be recycled using a fluorous/organic biphasic system.[2] The fluorinated phosphine ligand **1a** (Figure 1) employed in this reaction has two methylene groups between the phosphorus atom and the perfluoroalkyl moiety, so the electron-withdrawing effect of the perfluoroalkyl groups is suppressed. However, the reported synthetic methods for **1a** suffer from poor yields.[3] Although there are known synthetic routes to the perfluoroalkylated triaryl phosphine ligand **1b**, these methods involve multiple steps which make the synthesis and isolation time-consuming.[4] In contrast, much less attention has been paid to the phosphine **2**, in which a perfluoroalkyl group is directly linked to the phosphorus atom,[5] because the strong electron-withdrawing effect of the ligand is believed to degrade the catalytic activity. Inspired by two series of reactions we previously developed—photoinduced radical addition reactions of perfluoroalkyl iodide to carbon–carbon unsaturated bonds[6] and photoinduced radical addition reactions of diphosphine to alkynes[7]—we identified a convenient synthetic route to the phosphines **2**. This approach involves the photoinduced reaction of diphosphines with perfluoroalkyl iodides [Eq. (1)]. Herein, we report the fluorous affinity as well as the electronic properties of **2**, including its coordination ability. Furthermore, we discuss a cross-coupling reaction that uses **2** as a recyclable ligand.

$$\underset{\textbf{1a}}{[R_f(CH_2)_2]_3P} \qquad \underset{\textbf{1b}}{(p\text{-}R_fC_6H_4)_3P} \qquad \underset{\textbf{2}}{R_fR_2P}$$

Figure 1. Perfluoroalkylated phosphine ligands **1a**, **1b**, and **2**.

$$\underset{\textbf{3}}{R_f-I} + \underset{\textbf{4}}{R_2P-PR_2} \xrightarrow{h\nu} \underset{\textbf{2}}{R_fPR_2} \qquad (1)$$

Irradiation of a mixture of perfluorodecyl iodide **3a** (0.20 mmol) and tetraphenyldiphosphine **4a** (0.24 mmol) in $CDCl_3$ with a xenon lamp through Pyrex, under an inert atmosphere for 12 h, afforded (perfluorodecyl)diphenylphosphine (**2a**) in quantitative yield [Eq. (2)]. The complete consumption of **3a** was confirmed by ^{19}F NMR and ^{31}P NMR spectroscopy.

$$\underset{\substack{\textbf{3a}\\0.20\text{ mmol}}}{n\text{-}C_{10}F_{21}-I} + \underset{\substack{\textbf{4a}\\0.24\text{ mmol}}}{Ph_2P-PPh_2} \xrightarrow[CDCl_3,\text{ RT, 12 h}]{h\nu\ (\lambda > 300\text{ nm})} \underset{\substack{\textbf{2a}\\>99\%}}{n\text{-}C_{10}F_{21}PPh_2} \qquad (2)$$

To investigate the scope and limitations of the above-mentioned photoinduced reaction, we used several perfluoroalkyl iodides with diphosphines (Table 1). Linear perfluoroalkyl iodides (**3a**–**d**) reacted with **4a** to afford the perfluoroalkyldiphenylphosphines **2a**–**d** quantitatively. Treatment of **2a**–**d** with S_8 and purification by silica gel column chromatography afforded the perfluoroalkyldiphenylphosphine sulfides **5a**–**d** in good yields (entries 1–4). Secondary iodides such as perfluorocyclohexyl iodide (**3e**) and perfluoroisopropyl iodide (**3f**), as well as ω-diiodides such as 1,6-diiodoperfluorohexane (**3g**) and 1,4-diiodoperfluorobutane (**3h**), gave the corresponding phosphine sulfides **5e**–**h** in good yields (entries 5–8). Tetrakis(*tert*-butyl)diphosphine (**4b**) could also be employed successfully to synthesize the desired perfluoroalkylated phosphine (entry 9).[8]

The perfluoroalkylated phosphines **2** were not readily oxidized in air (into the corresponding phosphine oxides) but were partly oxidized during purification by silica gel or alumina column chromatography. Therefore, an appropriate isolation method which prevents the oxidation of **2** had to be chosen. We attempted to isolate (perfluorodecyl)diphenylphosphine (**2a**) from the reaction system by using a fluorous/organic biphasic system (Figure 2), as this phosphine has a long-chain perfluoroalkyl group.[1a,2] To the mixture of the product and phosphorus residue ($Ph_2P(O)H$, $Ph_2P(O)OH$, etc.) in the reaction flask, MeOH (organic solvent) and Fluorinert (FC-72: perfluorohexanes; fluorous solvent) were added, and **2a** was isolated in 90% yield after the extraction

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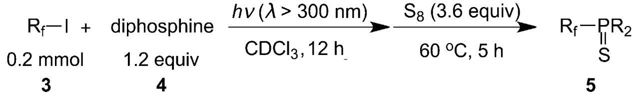
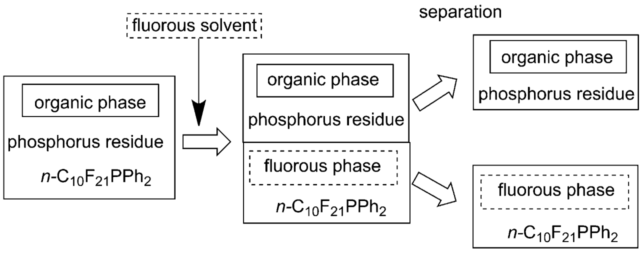
Table 1: Photoinduced reaction of perfluoroalkyl iodides with diphosphines.



$$\underset{\mathbf{3}}{\underset{0.2\ \text{mmol}}{R_f{-}I}} + \underset{\mathbf{4}}{\underset{1.2\ \text{equiv}}{\text{diphosphine}}} \xrightarrow[\text{CDCl}_3,\ 12\ \text{h}]{h\nu\,(\lambda > 300\ \text{nm})} \xrightarrow[60\ ^\circ\text{C},\ 5\ \text{h}]{S_8\ (3.6\ \text{equiv})} \underset{\mathbf{5}}{R_f{-}\overset{}{\underset{\|\atop S}{P}}R_2}$$

Entry	3	4	5	Yield [%][a]
1	**3a**: n-$C_{10}F_{21}$-I	**4a**: $(Ph_2P)_2$	**5a**: n-$C_{10}F_{21}$-P(S)Ph_2	80 (>99)
2	**3b**: n-C_8F_{17}-I	**4a**	**5b**: n-C_8F_{17}-P(S)Ph_2	88 (>99)
3	**3c**: n-C_6F_{13}-I	**4a**	**5c**: n-C_6F_{13}-P(S)Ph_2	86 (>99)
4	**3d**: n-C_4F_9-I	**4a**	**5d**: n-C_4F_9-P(S)Ph_2	85 (>99)
5	**3e**: c-C_6F_{11}-I	**4a**	**5e**: c-C_6F_{11}-P(S)Ph_2	89 (>99)
6	**3f**: $(CF_3)_2CF$-I	**4a**	**5f**: $(CF_3)_2CF$-P(S)Ph_2	60 (>99)
7[b]	**3g**: I-$(CF_2)_6$-I	**4a**	**5g**: $Ph_2P(S)$-$(CF_2)_6$-P(S)Ph_2	78 (>99)
8[b]	**3h**: I-$(CF_2)_4$-I	**4a**	**5h**: $Ph_2P(S)$-$(CF_2)_4$-P(S)Ph_2	76 (>99)
9[c]	**3a**	**4b**: $(tBu_2P)_2$	**5i**: n-$C_{10}F_{21}$-P(S)$t$$Bu_2$	53 (>99)

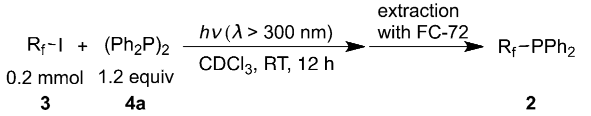
[a] Yield of product isolated after purification by silica gel column chromatography. The yields in parentheses were determined by ^{31}P or ^{19}F NMR spectroscopy. [b] The diphosphine **4a** (2.4 equiv) was used. After photoirradiation, the mixture was treated with S_8 (7.2 equiv) for 12 h. [c] After photoirradiation, the mixture was treated with S_8 for 36 h.



phosphorus residue : $Ph_2P(O)H$, $Ph_2P(O)OH$, etc.

Figure 2. Isolation by using fluorous biphasic system.

Table 2: Extraction of perfluoroalkylated phosphines using a fluorous biphasic system.



$$\underset{\mathbf{3}}{\underset{0.2\ \text{mmol}}{R_f\text{-I}}} + \underset{\mathbf{4a}}{\underset{1.2\ \text{equiv}}{(Ph_2P)_2}} \xrightarrow[\text{CDCl}_3,\ \text{RT},\ 12\ \text{h}]{h\nu\,(\lambda > 300\ \text{nm})} \xrightarrow{\substack{\text{extraction}\\ \text{with FC-72}}} \underset{\mathbf{2}}{R_f{-}PPh_2}$$

Entry	3	2	Yield [%][a]
1	**3a**: n-$C_{10}F_{21}$-I	**2a**: n-$C_{10}F_{21}$-PPh_2	90 (>99)[b]
2	**3j**: n-$C_{12}F_{25}$-I	**2j**: n-$C_{12}F_{25}$-PPh_2	94 (>99)[b]
3	**3b**: n-C_8F_{17}-I	**2b**: n-C_8F_{17}-PPh_2	41 (>99)[b]
4	**3c**: n-C_6F_{13}-I	**2c**: n-C_6F_{13}-PPh_2	19 (>99)[b]

[a] Isolation by extraction with Fluorinert (FC-72). [b] The yields in parentheses are determined by ^{31}P or ^{19}F NMR spectroscopy before isolation.

(Table 2, entry 1).[9] The phosphorus residue, obtained from the reaction of Ph_2PI with MeOH or oxidation, was transferred to the organic layer. Furthermore, (perfluorododecyl)-diphenylphosphine (**2j**), which has a longer alkyl chain than does **2a** (entry 2), could be successfully isolated. However, the yields of the isolated (perfluorooctyl)diphenylphosphine (**2b**) and (perfluorohexyl)diphenylphosphine (**2c**), both of which have shorter chains than **2a**, were unacceptably low because of the poor partition of the compounds between MeOH and FC-72 (entries 3 and 4).

To effectively use the fluorous/organic extraction method for product separation, understanding of the partition coefficient is important. Hence, we investigated the partition coefficients for **2a** and **5a** between FC-72 and several organic solvents (Table 3).[10] The highest partition coefficient for **2a** (to FC-72) was observed when using a combination of MeOH and FC-72, but the partition coefficients for the phosphine sulfide **5a** were much lower. The partition coefficient for **2j**, which has a long perfluorinated alkyl chain, was sufficiently high for this compound to be separated by the aforementioned extraction method [n-$C_{12}F_{25}PPh_2$ (**2j**): MeOH/FC-72 = 1/5.00]. In contrast, the partition coefficient for **2b**, which has a shorter perfluorinated chain, was low [n-$C_8F_{17}PPh_2$ (**2b**): MeOH/FC-72 = 1/0.40]; therefore, the biphasic system could not be used for extraction.

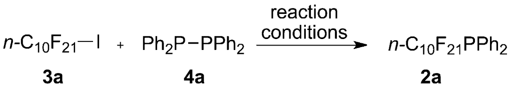
Table 3: Partition coefficients of the perfluoroalkylated compounds **2a** and **5a** between organic solvents and FC-72.[a]

Solvent	2a	5a
MeOH	1/1.17	1/0.36
acetone	1:0.28	1/0.12
AcOEt	1/0.16	1/0.05
$CHCl_3$	1/0.27	1/0.05
benzene	1/0.40	1/0.05

[a] Partition coefficients given for organic solvent/FC-72; values determined by gravimetric method.

The photoinduced reaction of diphosphines with perfluoroalkyl iodides was performed under several conditions to elucidate the reaction mechanism (Table 4). The reaction of **3a** with **4a** did not proceed under dark conditions (entry 1), but was successful in the presence of the radical initiator AIBN (1.3 equiv; entry 2), thus indicating that the mechanism involved a radical pathway. Intriguingly, the reaction of **3a** with **4a** also proceeded adequately under sunlight conditions (entry 3).

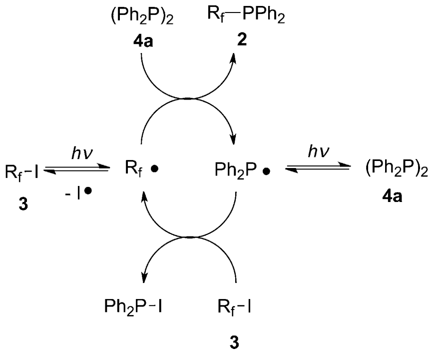
Table 4: Reaction of diphosphine with perfluoroalkyl iodide under different reaction conditions.



$$\underset{\mathbf{3a}}{n\text{-}C_{10}F_{21}{-}I} + \underset{\mathbf{4a}}{Ph_2P{-}PPh_2} \xrightarrow{\substack{\text{reaction}\\ \text{conditions}}} \underset{\mathbf{2a}}{n\text{-}C_{10}F_{21}PPh_2}$$

Entry	Reaction conditions	Yield [%]
1	dark, $CDCl_3$, RT, 12 h	8[a]
2	AIBN (1.3 equiv), C_6H_6, 80 °C, 6 h	90[b]
3[c]	sunlight, $CDCl_3$, RT, 10 h	91[b]

[a] Determined by ^{31}F NMR spectroscopy. [b] Yield of product isolated by fluorous/organic biphase system. [c] 0.70 mmol of **3a** was used. For detailed reaction conditions, see the Supporting Information.

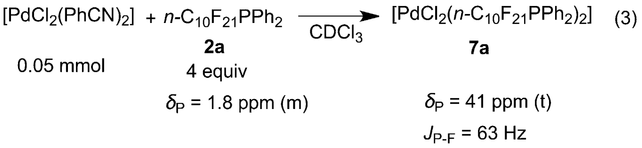


Scheme 1. A plausible reaction pathway for the photoinduced reaction of diphosphines with perfluoroalkyl iodides.

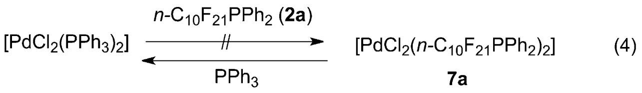
A plausible pathway for the present reaction is shown in Scheme 1. The absorption maxima (λ_{max}) of the perfluoroalkyl iodides and tetraphenyldiphosphine are 270 nm[6] and 260 nm,[11] respectively, and the absorption reaches the near-UV region. Therefore, near-UV light irradiation would induce bond cleavage in the perfluoroalkyl iodide and the diphosphine. The perfluoroalkyl radical generated by the cleavage of perfluoroalkyl iodide reacts with the diphosphine to form the perfluoroalkyl phosphine **2** and a phosphine radical. This radical, which can also be formed by the cleavage of tetraphenyldiphosphine upon near-UV light irradiation, abstracts an iodine atom from the perfluoroalkyl iodide to regenerate a perfluoroalkyl radical along with an iodophosphine species, which is finally converted into phosphorous residues such as $Ph_2P(O)H$ and $Ph_2P(O)OH$ during workup.[12]

Next, we investigated the electronic properties of **2** because they actually estimate the efficiency of the transition-metal catalyst. The perfluoroalkyl group in **2** is directly substituted at the phosphorus atom and hence may have a marked electronic effect.[13] The ^{31}P-^{77}Se coupling constant ($^1J_{P\text{-}Se}$) is known to be correlated with the electronic properties of the phosphine, that is, a large $^1J_{P\text{-}Se}$ value reflects the poor electron-donating ability of the phosphine.[14] Hence, we measured $^1J_{P\text{-}Se}$ for several phosphines (see Table S1 in the Supporting Information). Tertiary phosphines reacted readily with selenium in refluxing chloroform or toluene solution to form the corresponding phosphine selenides **6** (see the Supporting Information for structures). The $^1J_{P\text{-}Se}$ values of the perfluoroalkylated phosphines selenides were much larger than those of $Ph_3P{=}Se$ and $(p\text{-}CF_3C_6H_4)_3P{=}Se$, thus implying that the perfluoroalkylated phosphines are electron deficient.

The phosphine **2a**, despite its electron-poor nature, underwent a ligand exchange reaction with the benzonitrile unit of bis(benzonitrile)palladium(II) dichloride. In the ^{31}P NMR spectrum of a mixture of bis(benzonitrile)palladium(II) dichloride and **2a**, the signal representative of **2a** ($\delta_P = 1.8$ ppm) disappeared and a new signal ($\delta_P = 41$ ppm), attributable to bis(perfluorodecyldiphenylphosphine)palladium(II)dichloride (**7a**), appeared [Eq. (3)]. ^{31}P NMR analysis also indicated that the **2a** ligand in **7a** was quantitatively replaced by PPh_3 because of the weaker coordination ability of **2a** as compared to PPh_3. By contrast, the addition of **2a** to bis(triphenylphosphine)palladium(II) dichloride did not result in any such ligand exchange [Eq. (4)].



$$[PdCl_2(PhCN)_2] + n\text{-}C_{10}F_{21}PPh_2 \xrightarrow[CDCl_3]{} [PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2] \quad (3)$$



$$[PdCl_2(PPh_3)_2] \underset{PPh_3}{\overset{n\text{-}C_{10}F_{21}PPh_2\ (\mathbf{2a})}{\rightleftarrows}} [PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2] \quad (4)$$

We also succeeded in obtaining single crystals of **7a** for X-ray crystallography analysis.[15] The structure of **7a** is shown in Figure 3. Interestingly, **7a** adopted the *trans* conformation in the solid state, and the perfluoroalkyl groups were oriented in the same direction. Figure S1 (see the Supporting Information) revealed intermolecular stacking through the perfluoroalkyl groups. These unique results are attributed to the introduction of a long perfluoroalkyl chain into the ligand molecule.

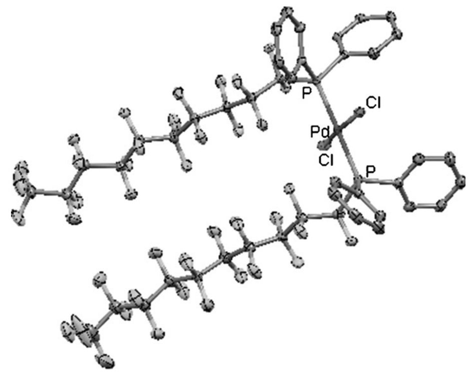
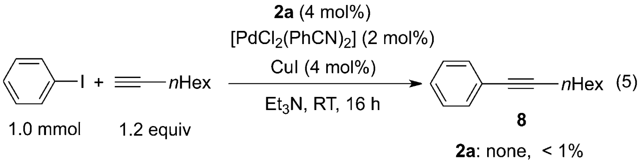
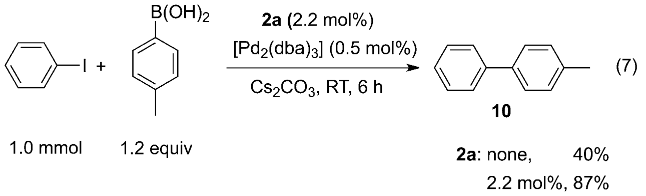


Figure 3. ORTEP representation (thermal ellipsoids at 50% probability) of **7a**. $R = 0.0346$, $R_w = 0.1059$, GOF = 1.132.

Finally, we demonstrated a number of coupling reactions that use **2a** as a recyclable ligand for the palladium catalyst. Although Sonogashira coupling[16] proceeded in the presence of **2a** to give the coupling product **8** in quantitative yield, no reaction occurred in the absence of **2a** [Eq. (5)].[17] The Mizoroki–Heck[18] and Suzuki–Miyaura coupling[19] reactions also proceeded efficiently in the presence of **2a** [Eqs. (6) and (7); dba = dibenzylideneacetone]. These results indicated that **2a** plays a vital role in the reactions. The recyclability of **2a** from the reaction systems was also investigated on the



2a: none, < 1%
4 mol%, 99%



basis of its fluorous affinity[20] (Table 5). After completion of the coupling reactions, the ligand was recovered by using a fluorous/organic biphasic system and reused five times for the same coupling reactions. The results showed that there was no appreciable loss of activity of **2a** for up to five runs.

Table 5: Recyclability of the ligand **2a** for several coupling reactions.

	Without **2a**	1st run with **2a**	1st recycle	2nd recycle	3rd recycle	4th recycle
Yield of **8**[a]	<1%	99%	99%	99%	99%	98%
Yield of **9**[b]	18%	87%	87%	89%	88%	83%
Yield of **10**[b]	40%	87%	98%	85%	–[c]	–[c]

[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopy. [c] Not measured.

In conclusion, we have developed a convenient synthetic route to perfluoroalkyl-substituted phosphines from diphosphines and perfluoroalkyl iodides. We proposed that this reaction proceeds by a photoinduced radical pathway. The affinity of long-chain ($\geq C_{10}$) perfluoroalkylated phosphines to fluorous solvents was sufficiently high. Hence, these phosphines could be easily separated using a fluorous biphasic system. The perfluoroalkyldiphenylphosphine **2a**, notwithstanding its poor electron-donating ability, formed a complex with palladium(II) and the resulting complex **7a** showed a unique conformation and packing. Furthermore, **2a** successfully promoted a number of coupling reactions and could be recycled using a fluorous/organic biphasic system. Future studies focusing on unique metal-catalyzed reactions in the presence of this easily accessible ligand are being planned.

Experimental Section

The general procedure for the synthesis of perfluoroalkyldiphenyl phosphines was as follows. Under an inert atmosphere, diphosphine (0.24 mmol), perfluoroalkyl iodide (0.20 mmol), and degassed $CDCl_3$ (600 μL) were placed in a sealed NMR tube (Pyrex). The mixture was vortexed for 30 s and then irradiated with a xenon lamp (500 W) at room temperature for 12 h. When degassed MeOH (5 mL) was added to the mixture after completion of the reaction, and Ph_2PI was converted into $Ph_2P(O)H$, $Ph_2P(O)OH$, and other phosphorus residues, along with some MeI. The solvents and MeI were then evaporated, and the residue was extracted with MeOH (4 mL) and Fluorinert (FC-72) (4 mL × 3) in a glove box. Subsequent evaporation of the fluorous layer afforded the pure perfluoroalkyldiphenyl phosphine. Further details of the experimental procedures and characterization data for the new compounds are included in the Supporting Information.

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Keywords: fluorinated ligands · phosphane ligands · photochemistry · radical reactions · synthetic methods

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[8] The yield of the isolated product in this entry is relatively low because HPLC for the separation of **5i** from several phosphine sulfides was carried out after silica gel column chromatography.

[9] Because the perfluoroalkyl iodide was completely consumed after photoirradiation, only the perfluoroalkyldiphenylphosphine was isolated.

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