The synthesis of tris(perfluoroalkyl)phosphines†

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Tris(perfluoroalkyl)phosphines, of interest as tunable alternatives to the carbon monoxide ligand, can be synthesised by the nucleophile mediated reaction of perfluoroalkyltrimethylsilanes with triphenylphosphite; the method can be extended to diphosphines.

The ability to systematically modify ligand properties is a desirable goal in ligand design. It is through the modification of the steric and electronic properties of attached ligands that the characteristics of metal complexes can be finely tuned in a predictable manner. This capacity for property modulation is a key attribute for organometallic and coordination complexes and is particularly important when considering their potential applications such as homogeneous catalysts. There is already a wide array of available electron-rich ligands amenable to modification. With moderately electron-withdrawing ligands, the options are much more limited.[1] The situation is worse, however, for strongly electron-withdrawing ligands. With ligands of equivalent π-acceptor strength to carbon monoxide, no tunable alternatives have yet emerged.[2] Thus, although carbon monoxide is one of the most important and versatile ligands in transition metal chemistry, and one of the few ligands capable of stabilising metals in positive, zero, or negative oxidation states, it cannot be modified. Other prototypical strong π-acceptor ligands, for example NO[3] and PF_3,[4] also lack a suitable "handle" for modification. Perfluoroalkylphosphines, however, possess both these attributes, since as π-acceptors they are as strong as CO[5] and yet they do have the "handle" intrinsic to phosphine ligands.

Tris(trifluoromethyl)phosphine was first prepared over 50 years ago in a seminal piece of work by the Emeléus group.[6] Despite several inherent drawbacks, this route has remained the method of choice for synthesising tris(trifluoromethyl)phosphine, since subsequent methods have involved the use of more hazardous reagents.[7] Unfortunately, the Emeléus synthesis does not work for longer chain tris(perfluoroalkyl)phosphines.[8] As a result, perfluoroalkylphosphines have remained a curiosity.[9,10] There is, therefore, a need for a convenient laboratory scale synthesis of perfluoroalkylphosphines. We sought to develop a simple and efficient procedure.

Ruppert's reagent, CF_3SiMe_3, has been widely used as a trifluoromethylating agent to introduce CF_3 groups into organic compounds. It has also been shown that this reagent could be used to create P–CF_3 groups from P–F,[11] P–CN[12] and P–$OC_6H_4NO_2$[13] linkages. To date, however, these strategies have not been successfully applied to the synthesis of tris(perfluoroalkyl)phosphines, $P(R_f)_3$ ($R_f = C_nF_{2n+1}$). We now report that not only CF_3SiMe_3, but other R_fSiMe_3 compounds can be used to synthesise $P(R_f)_3$ from triphenylphosphite [eqn (1)]. In addition, we show that this method can easily be extended to previously difficult to synthesise (fluoroalkyl)diphosphines.

$$\begin{gathered} P(OPh)_3 + 3R_fSiMe_3 \xrightarrow{CsF} P(R_f)_3 + 3PhOSiMe_3 \\ R_f = CF_3, C_2F_5, C_3F_7, C_4F_9 \end{gathered} \tag{1}$$

The results of our study are summarised in Table 1. Reaction of $P(OPh)_3$ with 3 equivalents of CF_3SiMe_3 in the presence of 3 equivalents of CsF at 25 °C produced $P(CF_3)_3$ in 98% yield. Under the same conditions, $C_2F_5SiMe_3$ gave $P(C_2F_5)_3$ also in high yield (Table 1, entry 3). The reactions with n-$C_3F_7SiMe_3$, and n-$C_4F_9SiMe_3$ were considerably slower and gave the corresponding extended chain tris(perfluoroalkyl)phosphines in reduced yields (Table 1, entries 7, 8). The extended chain compounds, $P(C_3F_7)_3$, $P(C_4F_9)_3$ and $P(C_6F_{13})_3$ could be made in high yield, however, by replacing $P(OPh)_3$ with the more reactive phosphite, $P(O$-p-$C_6H_4CN)_3$ (Table 1, entries 9–11). The same procedure could also be applied to the synthesis of arylbis(perfluoralkyl)phosphines and diarylperfluoroalkylphosphines[14,15] (Table 1, entries 12–15).

Of particular interest was the extension of the procedure to perfluoroalkyl substituted diphosphines [eqn (2)]. $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (**1**), a ligand used extensively by the Roddick group, has previously been synthesised by the potentially hazardous reaction of C_2F_5Li with $Cl_2PCH_2CH_2PCl_2$.[16] Reaction of $(PhO)_2PCH_2CH_2P(OPh)_2$[17] with 4 equivalents of R_fSiMe_3 (R_f = CF_3, C_2F_5) in the presence of CsF gave **1** and $(CF_3)_2PCH_2CH_2P(CF_3)_2$ in good yields (Table 1, entries 16, 17).[18]

$$\begin{gathered} (PhO)_2PCH_2CH_2P(OPh)_2 + 4R_fSiMe_3 \xrightarrow{CsF} \\ (R_f)_2PCH_2CH_2P(R_f)_2 + 4PhOSiMe_3 \\ R_f = CF_3, C_2F_5 \end{gathered} \tag{2}$$

No reaction was observed between $P(OPh)_3$ and R_fSiMe_3 (R_f = CF_3, C_2F_5) in the absence of an initiator. With only 0.1 equivalents of CsF however, $P(CF_3)_3$ and $P(C_2F_5)_3$ were formed in high yield (Table 1, entries 2, 4), demonstrating that the reaction is catalytic in CsF. Other sources of F^- and, indeed, alkoxides were found to be effective catalysts. Clearly, the observation that NaOPh, for example, is an effective catalyst indicates that P–F intermediates are not implicit in the reaction mechanism. A catalytic cycle is proposed in Scheme 1. In all examples of the reaction, $PhOSiMe_3$ was observed as a co-product.

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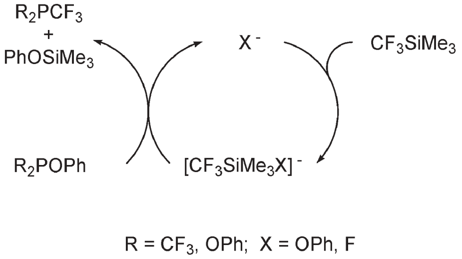
Table 1 Preparation of perfluoroalkylphosphines

Entry	Phosphite	Silane	Initiator	Phosphite:silane:initiator	Solvent	Product	Yield (%)[a,b]
1	$P(OPh)_3$	CF_3SiMe_3	CsF	1:3:3	Et_2O	$P(CF_3)_3$	98 (80)
2	$P(OPh)_3$	CF_3SiMe_3	CsF	1:3:0.1	Et_2O	$P(CF_3)_3$	90
3	$P(OPh)_3$	$C_2F_5SiMe_3$	CsF	1:3:3	Et_2O	$P(C_2F_5)_3$	98 (85)
4	$P(OPh)_3$	$C_2F_5SiMe_3$	CsF	1:3:0.1	Et_2O	$P(C_2F_5)_3$	95
5	$P(OPh)_3$	$C_2F_5SiMe_3$	NaOPh	1:3:0.5	Et_2O	$P(C_2F_5)_3$	75
6	$P(OPh)_3$	$C_2F_5SiMe_3$	TBAT[c]	1:3:0.5	Et_2O	$P(C_2F_5)_3$	45
7	$P(OPh)_3$	$C_3F_7SiMe_3$	CsF	1:3:0.5	PhCN	$P(C_3F_7)_3$	35
8	$P(OPh)_3$	$C_4F_9SiMe_3$	CsF	1:3:3	Et_2O	$P(C_4F_9)_3$	20
9	$P(O\text{-}p\text{-}C_6H_4CN)_3$	$C_3F_7SiMe_3$	CsF	1:3:0.5	Et_2O–PhCN	$P(C_3F_7)_3$	90
10	$P(O\text{-}p\text{-}C_6H_4CN)_3$	$C_4F_9SiMe_3$	CsF	1:3:3	Et_2O–PhCN	$P(C_4F_9)_3$	90 (40)
11	$P(O\text{-}p\text{-}C_6H_4CN)_3$	$C_6F_{13}SiMe_3$	CsF	1:3:3	Et_2O–PhCN	$P(C_6F_{13})_3$	90
12	Ph_2POPh	CF_3SiMe_3	CsF	1:1:0.5	Et_2O	Ph_2PCF_3	90
13	Ph_2POPh	$C_2F_5SiMe_3$	CsF	1:1:0.5	Et_2O	$Ph_2PC_2F_5$	98 (80)
14	$PhP(OPh)_2$	CF_3SiMe_3	CsF	1:2:0.1	Et_2O	$PhP(CF_3)_2$	90
15	$PhP(OPh)_2$	$C_2F_5SiMe_3$	CsF	1:2:0.1	Et_2O	$PhP(C_2F_5)_2$	90
16	$(PhO)_2PCH_2CH_2P(OPh)_2$	CF_3SiMe_3	CsF	1:4:4	Et_2O	$(CF_3)_2PCH_2CH_2P(CF_3)_2$	95
17	$(PhO)_2PCH_2CH_2P(OPh)_2$	$C_2F_5SiMe_3$	CsF	1:4:4	Et_2O	$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$	90

[a] Yield calculated *via* integration of one scan ^{31}P and ^{19}F NMR spectra. [b] Isolated yields in parentheses. [c] Tetrabutylammonium triphenyldifluorosilicate.



Scheme 1

In conclusion, we have developed a general and high yield procedure for the conversion of $P(OPh)_3$ into the corresponding $P(R_f)_3$ by reaction with R_fSiMe_3. The commercial availability and relatively non-hazardous nature of the reagents make the procedure a highly attractive alternative to the previously reported syntheses of tris(perfluoroalkyl)phosphines and bis(diperfluoroalkylphosphino)ethanes.

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