Trimethylsilyl- and Trimethylstannyldimethylphosphane—Convenient and Versatile Reagents for the Synthesis of Polyfluoroaryldimethylphosphanes

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Abstract: Trimethylsilyldimethylphosphane (Me_3SiPMe_2) and the corresponding tin compound (Me_3SnPMe_2) were used as reagents for the substitution of fluorine by the Me_2P group in polyfluoroarenes C_6F_5X (X = F, H, Cl, CF_3) and C_5NF_5. The reactions occur even under mild conditions ($T = 0-20\,^\circ C$), either in benzene or without solvent, to give as a rule 4-X-1-(dimethylphosphano)tetrafluorobenzenes ($XC_6F_4PMe_2$, **1**–**4**) and 4-(dimethylphosphano)tetrafluoropyridine ($C_5NF_4PMe_2$, **5**), respectively, in yields between 75 and 95%. In the case of C_6F_6, double substitution is also observed, which affords 1,4-bis(dimethylphosphano)tetrafluorobenzene (**6**). A very efficient route to the compounds $XC_6F_4PMe_2$ (X = F, H, Cl, CF_3) and $C_5NF_4PMe_2$ was developed as a one-pot reaction of the corresponding fluoroarenes with tetramethyldiphosphane (P_2Me_4) and trimethyltin hydride (Me_3SnH) at moderate temperatures. This process was tested for C_6F_6 and perfluorobiphenyl which gave $C_6F_5PMe_2$ (**1**) and 4,4′-bis(dimethylphosphano)octafluorobiphenyl (**7**), respectively. The results, which included kinetic measurements that used the intensities of the ^{31}P signals, revealed the influence of the substrate type on the rate of reaction in the sequence: $C_5NF_5 > C_6F_5CF_3 > C_6F_5Cl$, $C_6F_5PMe_2 > C_6F_5H > C_6F_6 \gg C_6H_5F$. Ab initio calculations were carried out on the model reactions of pentafluoropyridine with silylphosphane, phosphane or phosphide to discriminate between possible reaction mechanisms. The novel phosphanes were characterised by spectroscopic investigations (NMR, MS), by preparation of the related thiophosphanes $Ar_FP(=S)Me_2$ (**8**–**14**), their spectroscopic and analytic data and single crystal X-ray diffraction studies on five of these derivatives.

Keywords: ab initio calculations · arenes · fluorine · phosphanes · silyl reagents · stannyl reagents · structure elucidation

Introduction

The preparation of arylphosphanes by using arylhalides as precursors can be accomplished by various synthetic routes.[1] A particularly convenient procedure is the nucleophilic reaction of the chosen aryl halide with an alkali-metal phosphide, MPR_2, generated from the corresponding secondary phosphane, HPR_2, with phenyllithium,[2] potassium *tert*-butoxide[3] or hydroxide.[4] The nucleophiles MPR_2 may also be prepared through cleavage of triphenylphosphane with lithium, sodium or potassium.[5] This method, however, can be difficult experimentally owing to the high basicity of metal phosphides.

Therefore, the use of (trimethylsilyl)diphenylphosphane as nucleophile has been investigated in reactions with alkyl- or acylhalides to produce alkyl- or acyldiphenylphosphanes.[1] Reagents of this type, for example *tert*-butyl(isopropyl)- and *tert*-butyl(methyl)trimethylsilylphosphanes [(tBu)RPSiMe$_3$, R = iPr, Me] have recently been applied to convert such a reactive arylating agent as perfluoropyridine to the corresponding perfluoropyridylphosphanes.[6]

Since tertiary fluoroaryl- and fluoroalkylphosphanes are of interest as ligands in catalytically active transition metal complexes, due to their reduced σ-donor and enhanced π-acceptor properties,[7] we have studied the reactivity of (trimethylsilyl)dimethylphosphane, Me_3SiPMe_2, and the related tin compound, Me_3SnPMe_2, in combination with a variety of polyfluoroarenes and perfluoropyridine. Kinetic investigations were included to elucidate the reactivity as a

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function of different substituents X (X = H, Cl, CF_3, F, PMe_2) in C_6F_5X. To get some insight into the mechanism of the Me_2P transfer to polyfluoroarenes, theoretical calculations were carried out on plausible transition states.

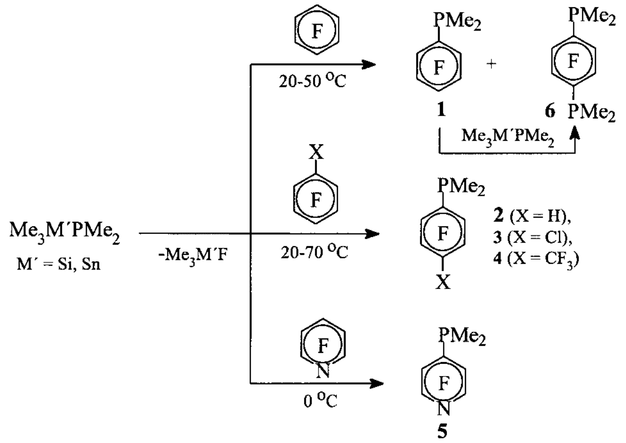
In this paper we report on the reactions of the abovementioned polyfluoroarenes with Me_3SiPMe_2 or Me_3SnPMe_2 and the derivatisation of the resulting phosphanes to the corresponding thiophosphanes.

Results and Discussion

In view of the air and moisture sensitivity of the phosphane reagents $Me_3M'PMe_2$ (M′ = Si, Sn) and the expected polyfluoroarylphosphane derivatives, high vacuum and Schlenk techniques were used for the experiments and for the characterisation of the products. This procedure is particularly convenient for the present study, because the starting compounds are relatively volatile substances, for example Me_3SiPMe_2 (b.p. 129 °C, 1013 mbar), C_6F_5Cl (b.p. 122–123 °C, 1013 mbar).

Preparation of the (polyfluoroaryl)dimethylphosphanes Ar_FPMe_2 and their sulfur derivatives $Ar_FP(=S)Me_2$: The reactions of the polyfluoroarenes with Me_3SiPMe_2 were carried out in sealed ampoules, as a rule by using the Ar_F compound in excess. Conditions and results are presented in Scheme 1. The rate of the reactions was followed by the time dependence of the yields estimated on the basis of the ^{31}P signal intensities of the products. These results are depicted in Figure 6–8 in the next section.

Abstract in German: *Trimethylsilyl-dimethylphosphan Me_3SiPMe_2 und die entsprechende Zinnverbindung Me_3SnPMe_2 wurden auf ihre Eignung als Reagenzien für die Substitution von Fluor in Polyfluorarenen C_6F_5X (X = F, H, Cl, CF_3) und C_5NF_5 durch Me_2P-Gruppen untersucht. Die Reaktionen laufen schon unter milden Bedingungen (T = 0–20 °C) ohne Lösungsmittel oder in Benzol ab und führen in der Regel in Ausbeuten zwischen 75 und 95 % zu den 4-X,1-(Dimethylphosphano)tetrafluorbenzolen $XC_6F_4PMe_2$ (**1–4**) bzw. zu 4-Dimethylphosphano-tetrafluorpyridin $C_5NF_4PMe_2$ (**5**). Im Fall von C_6F_6 wird zusätzlich Zweifach-Substitution zum 1,4-(Dimethylphosphano)tetrafluorbenzol **6** beobachtet. Ein besonders günstiger Weg zu den Verbindungen **1–5** wurde mit der bei niedrigen Temperaturen ablaufenden Eintopf-Reaktion der entsprechenden Polyfluorarene mit Tetramethyldiphosphan P_2Me_4 und Trimethylzinnhydrid Me_3SnH entwickelt und für die Umsetzung von C_6F_6 bzw. Perfluorbiphenyl zu **1** bzw. 4,4′-Bis(dimethylphosphano)octafluorbiphenyl **7** überprüft. Die Ergebnisse kinetischer Messungen unter Nutzung der Signalintensitäten in den $^{31}P\{^1H\}$-NMR-Spektren der Reaktionsgemische lassen für den Einfluss der Polyfluorarene auf die Reaktionsgeschwindigkeit folgende Abstufung erkennen: $C_5NF_5 > C_6F_5CF_3 > C_6F_5Cl$, $C_6F_5PMe_2 > C_6F_5H > C_6F_6 \gg C_6H_5F$. Für die Modellreaktionen von Pentafluorpyridin mit Silylphosphan, Phosphan oder Phosphid wurden ab initio Rechnungen durchgeführt, um zwischen möglichen Reaktionsmechanismen zu unterscheiden. Die neuen Phosphanderivate wurden durch spektroskopische Untersuchungen (NMR, MS) und durch Derivatisierung zu den entsprechenden Thiophosphanen $Ar_FP(=S)Me_2$ (**8–14**), deren spektroskopische und analytische Daten sowie durch Röntgenbeugung an Einkristallen von fünf dieser Derivate charakterisiert.*



Scheme 1.

Me_3SiPMe_2 was found to react with all the polyfluoroarenes tested at an appreciable rate even at room temperature, either without solvent or in benzene, to give the corresponding phosphane derivatives **1–5**. The pentafluorobenzene precursors C_6F_5X (X = H, CF_3) regioselectively form the *para*-substituted derivatives $Me_2PC_6F_4X$ in high yields (75–95 %). In the case of C_6F_5Cl, the *ortho-* and *meta*-substituted derivatives $Me_2PC_6F_4Cl$ are also formed in yields of up to 11 and 3 %, respectively. With hexafluorobenzene, not only **1** is produced but also the product of its further conversion: *para*-bis(dimethylphosphano)tetrafluorobenzene (**6**). Evidently, the reaction of **1** with Me_3SiPMe_2 exhibits the same regioselectivity as is observed for the compounds C_6F_5X.[9] The formation of **5** from pentafluoropyridine, which reacts far more readily than the other substrates, is in accord with the regioselectivity reported for its reaction with (*t*Bu)RP-$SiMe_3$.[6]

The new polyfluoroarylphosphanes were isolated by fractional distillation. The molecular structures of **2–6**, which have been prepared for the first time, have been deduced from their ^1H, ^{19}F, ^{31}P NMR spectroscopy and MS data shown in Table 1 and in the Experimental Section, respectively. In particular, the ^{19}F chemical shifts and coupling constants are characteristic for the positions of the different fluorine nuclei with respect to the Me_2P substituent. Thus, the signals for the fluorine atoms *ortho* to the phosphano group are observed in the range $\delta_F = -136$ to -131 (relative to CCl_3F as external standard) and correspond to the literature data of the known derivative **1**.[8] The δ_F values of the F atoms *meta* to the Me_2P group are very close to those observed for the *ortho*-F substituents of the X group in C_6F_5X compounds.[8a]

Compounds **1–6** were also characterised by preparing the corresponding thiophosphane derivatives (**8–13**) through reaction with elemental sulfur under various conditions,

Table 1. ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR data of the dimethyl(polyfluoroaryl)phosphanes **1**–**7** and their sulfides **8**–**14**

compound	δ (J [Hz^{-1}])[a]				
	F^{2,6}	F^{3,5}	F^4 or CF$_3$	P	H
1[b]	– 132.0	– 163.0	– 154.4	– 48.53 (t, $^3J_{PF} = 30.0$)	1.23 (dt, $^2J_{PH} = 5.3$, $^5J_{FH} = 1.1$, 6H, CH$_3$)
2[b]	– 133.6	– 140.0		– 46.52 (t, $^3J_{PF} = 26.9$)	6.89 (q, $^3J_{FH} \sim {}^4J_{FH} = 8.3$, 1H, CH) 1.38 (d, $^2J_{PH} = 5.0$, 6H, CH$_3$)
3[c]	– 131.2	– 141.1		– 46.38 (t, $^3J_{PF} = 26.2$)	1.22 (d, $^2J_{PH} = 5.1$, 6H, CH$_3$)
4[c]	– 131.4	– 142.1	– 57.4 (t, $^4J_{FF} = 21.5$)	– 41.6 (tq, $^3J_{PF} = 20.9$, $^4J_{PF} = 1.4$)	1.42, (d, $^2J_{PH} = 5.0$, 6H, CH$_3$)
5[b]	– 136.0	– 94.4		– 38.7 (t, $^3J_{PF} = 12.5$)	1.60 (dt, $^2J_{PH} = 4.8$, $^5J_{FH} = 1.4$, 6H, CH$_3$)
6[b]	– 132.9			– 47.0	1.19 (d, $^2J_{PH} = 5.0$, 6H, CH$_3$)
7[b]	– 138.4	– 131.0		– 43.8	1.13 (dt, $^2J_{PH} = 5.2$, $^5J_{FH} = 1.6$, 6H, CH$_3$)
8[b]	– 132.4	– 159.5	– 149.1	27.69	1.61 (dt, $^2J_{PH} = 13.8$, $^5J_{FH} = 2.2$, 6H, CH$_3$)
9[b]	– 132.7	– 136.4		27.55 (q, $^3J_{PF} \sim {}^4J_{PF} = 3.9$)	6.14 (tt, $^3J_{FH} = 7.6$, $^4J_{FH} = 7.5$, 1H, CH); 1.55 (dt, $^2J_{PH} = 13.6$, $^5J_{FH} = 2.4$, 6H, CH$_3$)
10[b]	– 131.9	– 138.8		27.87 (q, $^3J_{PF} \sim {}^4J_{PF} = 4.3$)	1.60 (dt, $^2J_{PH} = 13.8$, $^5J_{FH} = 1.2$, 6H, CH$_3$)
11[b]	– 130.6	– 138.2	– 56.2 (t, $^4J_{FF} = 21.4$)	28.65 (q, $^3J_{PF} \sim {}^4J_{PF} = 4.6$)	1.56 (dt, $^2J_{PH} = 13.7$, $^5J_{FH} = 2.2$, 6H, CH$_3$)
12[b]	– 134.0	– 88.9		28.71 (q, $^3J_{PF} \sim {}^4J_{PF} = 4.7$)	1.52 (dt, $^2J_{PH} = 13.4$, $^5J_{FH} = 2.0$, 6H, CH$_3$)
13[d]	– 129.3 (s)			29.29 (s)	2.20 (d, $^2J_{PH} = 13.5$, 6H, CH$_3$)
14	– 135.2	– 130.8		28.17 (s)	1.53 (dt, $^2J_{PH} = 13.4$, $^5J_{FH} = 2.4$, 6H, CH$_3$)

[a] In all cases where signal structures are not defined, they are multiplets. [b] Solution in C$_6$D$_6$. [c] Pure form. [d] Solution in C$_6$D$_6$/C$_6$H$_6$.

either with or without solvents. The most effective and clean method was the direct reaction according to Equation (1).

$$Ar_FPMe_2 + \tfrac{1}{8}S_8 \longrightarrow Ar_FP(=S)Me_2 \qquad (1)$$

The novel derivatives were characterised by spectroscopic (NMR, MS) and elemental analysis (C, H, N). In addition to the spectroscopic data of **1**–**6**, the results prove the identity of the air-sensitive precursors. The spectroscopic data of **8**–**13** are shown in Table 1. Typical fragmentation patterns and the results of the elemental analysis are given in the Experimental Section. The thiophosphanes **9**, **10**, **12** and **13** together with the corresponding derivative **14** of the 4,4′-bis(dimethylphosphano)perfluorobiphenyl **7** (see Scheme 2) were also characterised by single crystal X-ray diffraction studies. The molecular structures are presented in Figures 1–5. Selected bond lengths and angles are given in Table 2 to evaluate the influence of the different Ar$_F$ substituents on the geometric data.

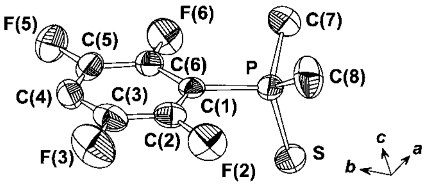


Figure 1. Molecular structure of **9**. Thermal ellipsoids are shown here at the 50% probability level. Hydrogen atoms have been omitted for clarity.

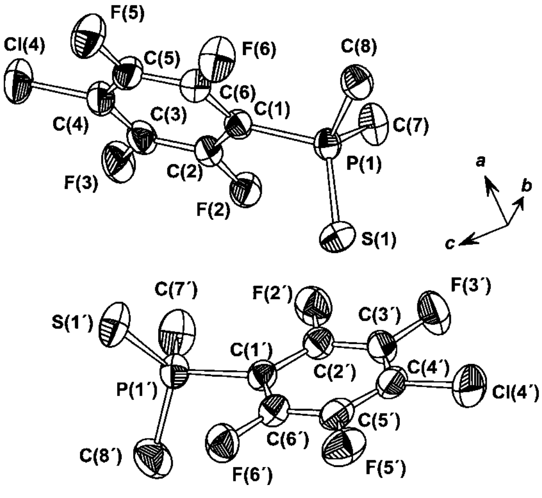
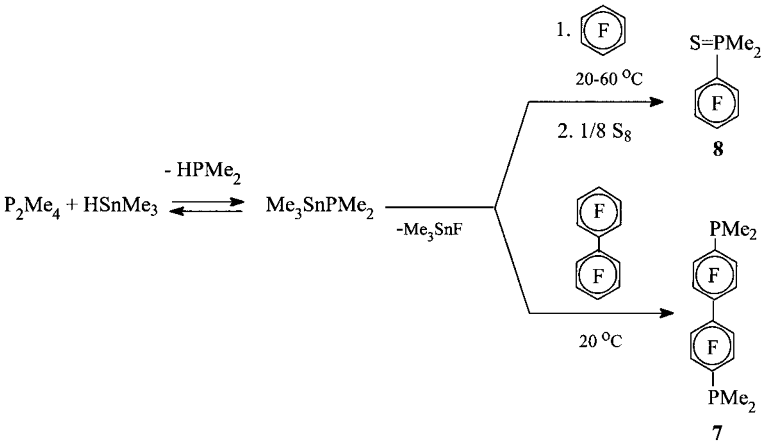


Figure 2. Molecular structure of **10**. Thermal ellipsoids are shown here at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Scheme 2.

The molecular structures of the compounds **9**, **10**, **12** and **13** are very similar; differences are due to the various building units CX or N in the *para*-position to the Me$_2$PS substituents. Besides **13**, which crystallises in the orthorhombic space group *Pccn*, the structures of **9**, **10** and **12** belong to the monoclinic space group $P2_1/c$. Compound **14** is a derivative of perfluorobiphenyl and contains the Me$_2$PS units in the 4- and 4′-positions. The planes of the benzene rings are tilted to each other by an angle of 51.8(1)° to reduce the repulsive interaction between the 2/2′- and 6/6′-fluorine atoms (in the crystallographic numbering of Figure 5: 3/3′- and 5/5′-positions). The influence of the CX or N ring units in the *para*-position to the Me$_2$PS group on the bond lengths and angles is small but significant. Thus the P–C(aryl) bond lengths vary from 1.833(2) Å (**9**) to 1.840(3) Å (**12**) and the P–S bond

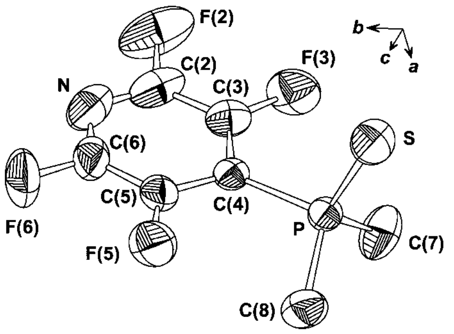


Figure 3. Molecular structure of **12**. Thermal ellipsoids are shown here at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

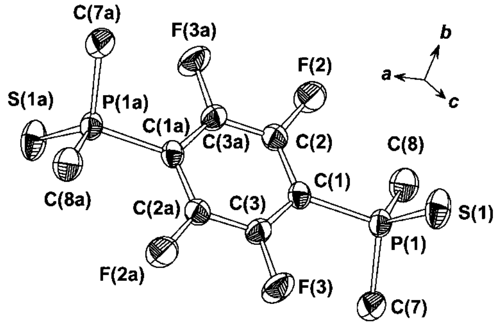


Figure 4. Molecular structure of **13**. Thermal ellipsoids are shown here at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

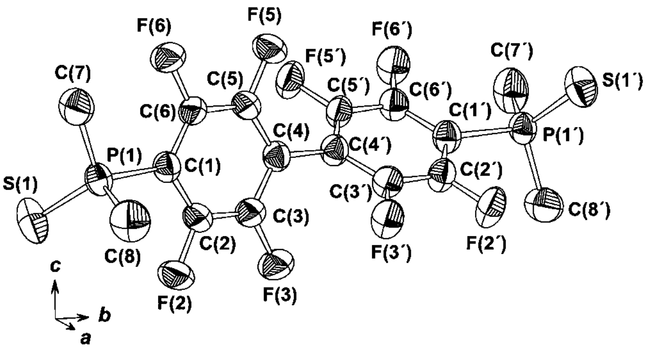


Figure 5. Molecular structure of **14**. Thermal ellipsoids are shown here at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

lengths follow the sequence **12** < **14** < **9** < **10** < **13**. The two pyramidal Me_2PS subunits in **13** and **14** contain the sulfur atoms in the crystal structures on opposite sides of the ring plane (**13**) or the best plane of the biphenyl skeleton (**14**).

Me_3SnPMe_2 also reacts with polyfluoroarenes at room temperature to yield basically the same substitution products as demonstrated for C_6F_6, C_6F_5H and C_6F_5Cl. However, unlike the mixtures formed in the reaction with Me_3SiPMe_2 which stay homogeneous, in this case poorly soluble polymeric Me_3SnF precipitates. With C_6F_5Cl, *ortho-* and *meta*-fluorine substitution was again observed in a total yield of about 14 %. The yield of **2** reached 60 % after 22 h at 20 °C—as compared with 60 h for Me_3SiPMe_2 (see curve c in Figure 6 below)—and increased to 92 % after 2 h at 60 °C. The same time was needed for the silylphosphane at 70 °C (see curve d in Figure 6). This means that the reactivity of the tin compound is approximately twice as great as that of the silicon analogue. The reaction was completed by further heating at 60 °C for 1 h and the phosphane **2** was transformed into the thiophosphane **9** in 63 % yield (see Experimental Section). Thus Me_3SnPMe_2 proved to be a very effective reagent for introducing Me_2P groups into fluoroarene compounds.

Table 2. Selected bond lengths [Å] and angles [°] of the compounds **9**, **10**, **12**–**14**

	9	**10**[a]	**12**	**13**	**14**
P−C(7)	1.784(2)	1.796(3) 1.793(4)	1.785(4)	1.795(2)	1.796(3) 1.797(3)
P−C(8)	1.781(2)	1.785(3) 1.800(4)	1.789(4)	1.788(2)	1.798(3) 1.797(3)
P−C(aryl)	1.833(2)	1.834(3) 1.836(3)	1.840(3)	1.838(2)	1.838(2) 1.845(2)
P−S	1.943(2)	1.945(1) 1.936(1)	1.937(1)	1.947(1)	1.940(1) 1.940(1)
C(7)-P-C(8)	103.4(3)	104.2(2) 104.5(2)	104.1(2)	103.8(2)	104.7(2) 104.6(2)
C(7)-P-S	114.6(2)	114.1(2) 113.7(2)	115.6(2)	114.1(1)	113.2(1) 114.4(1)
C(8)-P-S	114.8(2)	113.9(2) 114.8(2)	115.0(2)	114.3(1)	115.2(1) 114.1(1)
C(7)-P-C(aryl)	106.9(2)	104.8(2) 104.5(2)	105.1(2)	105.6(1)	107.8(1) 107.8(1)
C(8)-P-C(aryl)	106.3(1)	107.8(2) 103.5(2)	106.8(2)	107.4(1)	102.9(1) 103.9(1)
C(aryl)-P-S	110.1(1)	111.3(1) 111.3(1)	109.5(1)	111.0(1)	112.2(1) 111.3(1)

[a] Two independent molecules per unit cell.

Since this reagent is easily prepared by cleavage of the diphosphane P_2Me_4 with trimethyltin hydride Me_3SnH at room temperature, this result opens up a very convenient one-pot procedure for the preparation of Me_2P-substituted polyfluoroarenes according to Equation (2).

$$Me_3SnH + P_2Me_4 + C_6F_5X \longrightarrow Me_3SnF + Me_2PC_6F_4X + Me_2PH \qquad (2)$$

This route includes the in situ generation of the organotin precursor. Its usefulness was demonstrated by the preparation of **1**, its in situ conversion to the corresponding thiophosphane **8** and the preparation of 4,4′-bis(dimethylphosphano)octafluorobiphenyl (**7**) (Scheme 2). Compound **7** has been characterised on the basis of ^1H, ^{19}F, ^{31}P NMR spectroscopy and MS measurements. It was also converted to the corresponding sulfur derivative **14** and further investigated (NMR spectroscopy, MS, elemental analysis, X-ray diffraction).

In conclusion, both Me_3SiPMe_2 and Me_3SnPMe_2 are effective, convenient and versatile reagents for introducing Me_2P groups into polyfluoroarenes, C_6F_5X, by replacing the F atoms in the *para*-position to X. The more suitable reagent is Me_3SiPMe_2, because a very smooth reaction occurs under mild conditions; this affords almost exclusively (except for C_6F_6) the monosubstituted derivatives. In the case of C_6F_6, the monosubstituted compound is obtained by using a tenfold excess of C_6F_6, while the *para* disubstituted product **6** can be prepared in high yield by starting from a 2:1 molar ratio of Me_3SiPMe_2 and C_6F_6.

Mechanistic investigations of the reactions of polyfluoroarenes with Me_3SiPMe_2: To the best of our knowledge, the preparative results described above present the reagents $Me_3M'PMe_2$ (M′ = Si, Sn) for introducing Me_2P groups in the *para*-position to substituents X in polyfluoroarenes for the first time. Since these compounds contain both a nucleophilic centre at P and an electrophilic centre at Si or Sn, it was of special interest to investigate the reaction mechanism kinetically. The silicon compound was chosen for this study because it was used as the main preparative tool. The course of the reactions was monitored by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy, with the last one being the most convenient for the quantitative estimation of reagent and product concentrations. The results of the reactions with C_6F_5H are shown as kinetic curves in Figure 6. Curve a, which depicts the increase of the yield of **2** with time in relation to the initial amount of Me_3SiPMe_2 in benzene at 20 °C, is in complete agreement with curve b: the simultaneous decrease in Me_3SiPMe_2 concentration. There is no evidence for the formation of P_2Me_4 or any other side-product. After a reaction time of 500 h, Me_3SiPMe_2 was quantitatively converted to the desired product **2** (>97 %). As expected, the rate of reaction was somewhat higher in the absence of benzene, as demonstrated by curve c. Raising the temperature to 70 °C resulted in a considerable increase of the rate, curve d, without any change in the composition of the product mixture.

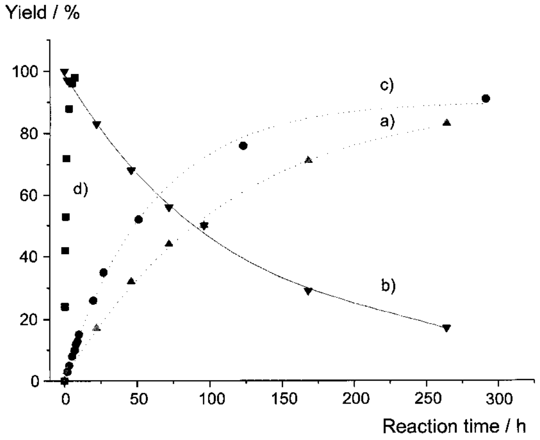


Figure 6. Time dependence of the yield of **2** in the reaction of pentafluorobenzene with Me_3SiPMe_2. Curve a) $[C_6F_5H]_0$ 1.3 mol L^{-1}, $[Me_3SiPMe_2]_0$ 1.0 mol L^{-1}; solution in benzene; 20 ± 1 °C. Curve b) The simultaneous decrease in Me_3SiPMe_2 concentration. Curve c) $[C_6F_5H]_0$ 4.4 mol L^{-1}; $[Me_3SiPMe_2]_0$, 3.1 mol L^{-1}; 20 ± 1 °C. Curve d) $[C_6F_5H]_0$ 4.4 mol L^{-1}, $[Me_3SiPMe_2]_0$ 3.1 mol L^{-1}; 70 ± 5 °C.

Similarly clear results were obtained for the reactions of Me_3SiPMe_2 with C_6F_5Cl in benzene (curve a in Figure 7) or without solvent, curve b. C_6F_5Cl reacted more quickly than C_6F_5H as shown by a comparison of curves e and a of Figure 7.

The reaction of hexafluorobenzene was found to be more complicated than that of C_6F_5H or C_6F_5Cl, because besides **1** the *para*-disubstituted derivative **6** is formed. Curve f in Figure 7 reflects the total augmentation of both **1** and **6** and, in comparison with curve a, reveals that fluorine in place of chlorine (C_6F_6 vs. C_6F_5Cl) reduces the rate of substitution. The individual changes in the yields of **1** and **6** are given in Figure 8 by the curves a and a′, respectively for the accumulation in benzene or by b and b′ for accumulation with a twofold amount of C_6F_6. In both cases the final yield of **6** (after ca. 200 h) reaches about 35 % and distinctly exceeds that of **1** (ca. 25 %). The degree of disubstitution can be reduced by increasing the initial molar ratio of C_6F_6:Me_3SiPMe_2; thus, with a tenfold amount of C_6F_6 the yields of **1** and **6** are 65 and 15 %, respectively, after 125 h at room temperature (curves c and c′ in Figure 8).

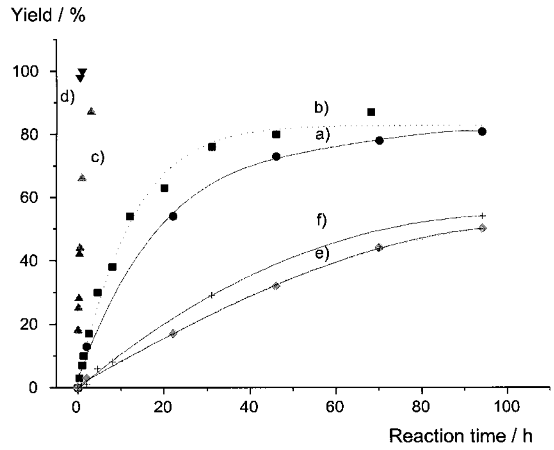


Figure 7. Time dependence of the yields of **1**–**4** and **6** in the reactions of C_6F_5X (X = H, Cl, F, CF_3) with Me_3SiPMe_2. Curve a) $[C_6F_5Cl]_0$ 2.1 mol L^{-1}, $[Me_3SiPMe_2]_0$ 1.4 mol L^{-1}; solution in benzene; 20 ± 1 °C. Curve b) $[C_6F_5Cl]_0$ 3.9 mol L^{-1}, $[Me_3SiPMe_2]_0$ 3.2 mol L^{-1}; 20 ± 1 °C. Curve c) $[C_6F_5Cl]_0$ 4.1 mol L^{-1}, $[Me_3SiPMe_2]_0$ 3.0 mol L^{-1}; 50 ± 5 °C. Curve d) $[C_6F_5CF_3]_0$ 2.0 mol L^{-1}, $[Me_3SiPMe_2]_0$ 1.4 mol L^{-1}. Curve e) $[C_6F_5H]_0$ 1.3 mol L^{-1}, $[Me_3SiPMe_2]_0$ 1.0 mol L^{-1}; solution in benzene; 20 ± 1 °C. Curve f) $[C_6F_6]_0$ 2.7 mol L^{-1}, $[Me_3SiPMe_2]_0$ 1.4 mol L^{-1}; solution in benzene; 20 ± 1 °C.

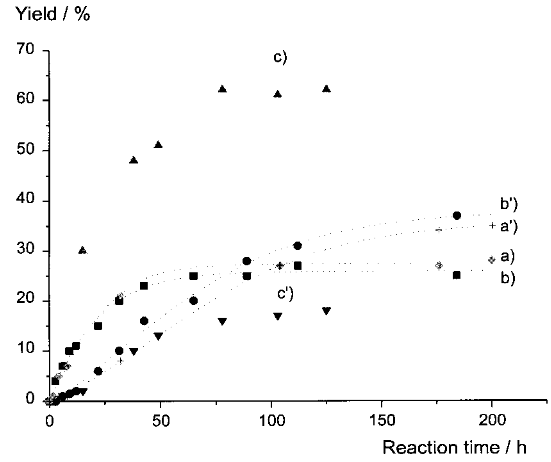


Figure 8. Time dependence of the yield of **1** (curves a, b, c) and **6** (curves a′, b′, c′) in the reaction of hexafluorobenzene with Me_3SiPMe_2. Curves a), a′) $[C_6F_6]_0$ 2.7 mol L^{-1}, $[Me_3SiPMe_2]_0$ 1.4 mol L^{-1}; solution in benzene; 20 ± 1 °C. Curves b), b′) $[C_6F_6]_0$ 5.7 mol L^{-1}, $[Me_3SiPMe_2]_0$ 2.9 mol L^{-1}; 18 ± 1 °C. Curves c), c′) $[C_6F_6]_0$ 8 mol L^{-1}, $[Me_3SiPMe_2]_0$ 0.8 mol L^{-1}; 18 ± 1 °C.

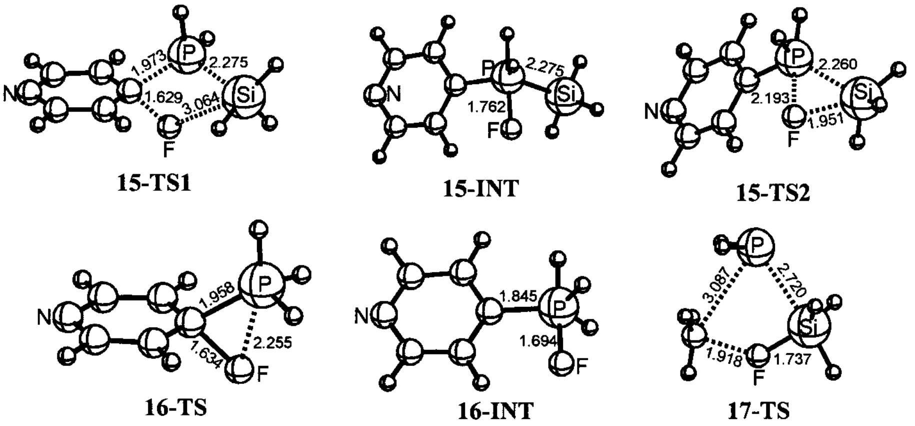
Since no other P-containing compounds are formed, the observed dependence of the product portions on the molar ratio of the reagents allows the preparation of **6** as the main product by decreasing the ratio C_6F_6:Me_3SiPMe_2 to 1:2. This could be demonstrated in a separate experiment, followed by the in situ sulfuration of **6**.

The rate of reaction is dramatically enhanced with increasing electron-withdrawing character of the substituent X in the substrates C_6F_5X in the series H, Cl, F < CF_3 (refer to curves a and d in Figure 7). The reactivity of pentafluoropyridine is even greater than that of the polyfluoroarenes C_6F_5X. It reacts vigorously with Me_3SiPMe_2 even on melting the reaction mixture at about 0 °C. As described for the corresponding reaction of pentafluoropyridine with *t*Bu(alk)PSiMe$_3$,[6] the process is highly exothermic and accompanied by a boiling up of the mixture due to the formation of the gaseous Me_3SiF (b.p. 19 °C, 973 mbar).

The kinetic data presented in Figures 6–8 were used to select optimal conditions for preparing individual compounds (see Experimental Section) and for evaluating rate constants for the second order reactions. The values $[1/(a-b)]\cdot\ln[b(a-x)/a(b-x)]$ show a linear dependence on the reaction time (t) with correlation coefficients of 0.97 to 0.99. Here, a and b are the initial concentrations of Me_3SiPMe_2 and C_6F_5X, respectively, and x indicates the amount of reagent converted during time t. The $k(PMe_2)$ values for the second step of the reaction of $C_6F_5PMe_2$ with the silylphosphane to give **6** were calculated by means of Equation (3), which relates the ratio of the rate constants for the successive/parallel reaction $[k(PMe_2)/k(F)] = \chi$ to the maximum concentration $[C_6F_5PMe_2]_{max}$ of the first product observed in the reaction course and the initial concentration of the substrate $[C_6F_6]_0$.[10]

$$(\chi)^{\chi/1-\chi} = \frac{[C_6F_5PMe_2]_{max}}{[C_6F_6]_0} \quad (3)$$

The rate constants $k(X) \times 10^6\,L\,mol^{-1}s^{-1}$ obtained for the reactions either in benzene at 20 °C or without solvent at 17–20 °C are: $k(Cl) = 4.8 \pm 1.0$ and 6.3 ± 1.3, $k(PMe_2) = 4.7 \pm 1.0$ and 3.1 ± 0.7, $k(H) = 2.2 \pm 0.4$ and 1.1 ± 0.2, $k(F) = 1.1 \pm 0.2$ and 0.6 ± 0.1. The values for $k(H)$ and $k(Cl)$ in the absence of solvent increase with increasing temperature to $k(H) = (8.2 \pm 1.6) \times 10^{-5}\,L\,mol^{-1}s^{-1}$ at 70 °C and $k(Cl) = (9.0 \pm 1.8) \times 10^{-5}\,L\,mol^{-1}s^{-1}$ at 50 °C (curve d in Figure 6 and curve c in Figure 7); this leads to a reasonable temperature coefficient of about 2.4. Thus, the influence of the substituent X on the reaction rate follows the sequence: $k(Cl) \approx k(PMe_2) > k(H) > k(F)$.



15-TS1 **15-INT** **15-TS2**

16-TS **16-INT** **17-TS**

Figure 9. B3LYP/6–31G(d)-optimised intermediates and transition structures in the model reactions (Table 3). Bond lengths are given in Å.

Monofluorobenzene was also tested as a substrate in the reaction with Me_3SiPMe_2, but did not show any activity up to 100 °C. At 180 °C, substitution took place in about 19, 37 and 60% yield after 6.5, 29 and 90 h, respectively. In conclusion, the reactivity of the investigated fluoroaromatic compounds follows the sequence: pentafluoropyridine > octafluorotoluene > pentafluoro-chlorobenzene > pentafluorobenzene > hexafluorobenzene ≫ fluorobenzene. In principle, this sequence corresponds to that which is observed for reactions of polyfluoroarenes with O-, S- and N-centred nucleophiles conventionally rationalised in terms of the S_NAr mechanism.[9] At first sight, there is no obvious reason why this mechanism should not operate in reactions of polyfluoroarenes with Me_3SiPMe_2. If this assumption can be verified, reagents of the type $Me_3M'PMe_2$ have to be qualified as nucleophiles of significantly lower reactivity than typical anionic representatives like sodium methoxide, but of higher reactivity than neutral agents such as piperidine.[11] This can be explained by the appreciable polarity of M'−P bonds and gains support from the observed activating effect of the polar solvent acetonitrile. Consequently, the Me_2P group in **1** displays a slight activating effect for the observed *para* substitution that affords **6**.

However, on the basis of the Lewis acid properties of silicon or tin centres in $R_3M'X$ compounds, an alternative pathway to the products Ar_FPMe_2 has to be considered. This starts with a nucleophilic attack of the *para* F atom at the acidic Si or Sn centre and leads to a four-membered transition state as shown in Figure 9 (see below), formula **15-TS1**. Last but not least, ionic or homolytic Si−P bond dissociation can be taken into account.[2, 12]

In order to discriminate between the possible routes, quantum-chemical calculations were carried out to determine the relative energies of different transition states and/or intermediates.

Quantum-chemical calculations: Ab initio model calculations[13] were performed to elucidate the mechanistic details of the reaction of (trimethylsilyl)dimethylphosphane with polyfluoroarenes. Earlier theoretical studies concerning the general mechanism of nucleophilic aromatic substitution reactions have used mainly semiempirical theory.[14] We have employed the hybrid density functional B3LYP with a standard Pople basis set [6–31G(d)]. All intermediates were fully optimised on the basis of semiempirically obtained (AM1) starting geometries. The stationary points were characterised as minima or transition structures by frequency calculations. The relative energies compared with the separated reactants are reported in Table 3; they include zero-point vibrational energies.

Firstly, we considered a concerted reaction of 4-fluoropyridine with silylphosphane, via a four-centre transition state **15-TS1**. The migration of the halogen atom towards the silicon

Table 3. Relative energies (B3LYP/6-31G(d)// B3LYP/6-31G(d) + ZPE) of the intermediates reported in the text.

	E_{rel} [kcal mol^{-1}]
4-fluoropyridine + H_3Si-PH_2	0.0
15-TS1	51.2
15-INT	9.1
15-TS2	11.1
4-pyridyl-phosphane + H_3Si-F	−26.9
4-fluoropyridine + PH_3	0.0
16-TS	+62.5
16-INT	+9.5
4-pyridyl-phosphane + HF	+15.1
CH_3F + H_3Si-PH_2	0.0
17-TS	+62.3
CH_3PH_2 + H_3Si-F	−37.1
4-fluoropyridine + PH_2^-	0.0
18-TS1	−1.9
18-INT1	−9.8
18-TS2	−9.4
18-INT2	−19.0
4-pyridyl-phosphane + F^-	+43.6
4-fluoropyridine + PH_2^- (ACN)[a]	0.0
18-TS1 (ACN)	+15.2
18-INT1 (ACN)	+7.3
18-TS2 (ACN)	+7.1
18-INT2 (ACN)	−1.6
4-pyridyl-phosphane + F^- (ACN)	+11.4
4-fluoropyridine + PH_2^- (BNZ)[b]	0.0
18-TS1 (BNZ)	+8.5
18-INT1 (BNZ)	−0.1
18-TS2 (BNZ)	0.0
18-INT2 (BNZ)	−9.0
4-pyridyl-phosphane + F^- (BNZ)	+24.0

[a] Acetonitrile ($\varepsilon = 36.64$). [b] Benzene ($\varepsilon = 2.247$)

occurs early on the reaction coordinate (Figure 9). However, the transition state exhibits a very long Si–F distance and also a very large barrier of more than 50 kcal mol^{-1}. This finding excludes a concerted, bimolecular one-step reaction between the aryl fluorides and the silylphosphane.

Secondly, when we examined the reaction between 4-fluoropyridine and PH_3, a similarly highly endoenergetic transition structure (**16-TS**) was found on the reaction path. The path continues with the migration of fluorine to the phosphorus atom; this leads to a pentacoordinated fluoro-4-pyridylphosphorane **16-INT**. The corresponding silyl-substituted intermediate **15-INT** is much lower in energy than the transition structure of the nucleophilic attack described above (**15-TS1**). Furthermore, **15-INT** is kinetically unstable and very prone to H_3Si-F elimination with a barrier of only 2 kcal mol^{-1} via **15-TS2**. This suggests that pentacoordinated phosphoranes are possible intermediates in the substitution reaction.

The high relative energies of **15-TS1** and **16-TS** are not specific to the aromatic system. In the reaction of CH_3F with H_3Si-PH_2, the transition structure **17-TS** is even higher in energy (62.3 kcal mol^{-1}), although the short Si–F bond length (1.737 Å) is supposed to lower the energy of the structure.[14]

As the approach of neutral phosphanes PR_3 to 4-fluoropyridine is repulsive, one might consider a third type of nucleophilic phosphorus species as reactant. In Figure 10 we show that the approach of the anion PH_2^- is indeed energetically preferred and may be responsible for the observed facile reaction under mild conditions. In the gas phase, no substantial barrier exists for the formation of a Meisenheimer complex **18-INT1** via **18-TS1**, which may result from a preceding weakly bound ion–dipole complex, which we have not searched for. The 1,2-migration of fluorine from carbon to phosphorus (**18-TS2**) is very facile ($E^{\neq} = 0.2$ kcal mol^{-1}). The tetracoordinated 4-pyridylfluorophosphanate **18-INT2** is the final intermediate from which F^- may be abstracted by the silyl cation, possibly after formation of the pentacoordinated **15-INT**.

Furthermore, we have calculated the free energies in solution for the five points on the coordinate of the last reaction according to the Self-Consistent Isodensity Polarisable Continuum Model (SCI-PCM) approach.[15] By using acetonitrile as a very dipolar solvent ($\varepsilon = 36.64$) in the model reaction, the relative energies of the species on the reaction path are all increased relative to the reaction of the unsolvated reactants. The barrier of 15.2 kcal mol^{-1} seems to be a realistic value for the rate-limiting step of the substitution reaction in solution. The Meisenheimer complex has reduced kinetic stability in solution and easily rearranges to **18-INT2**.

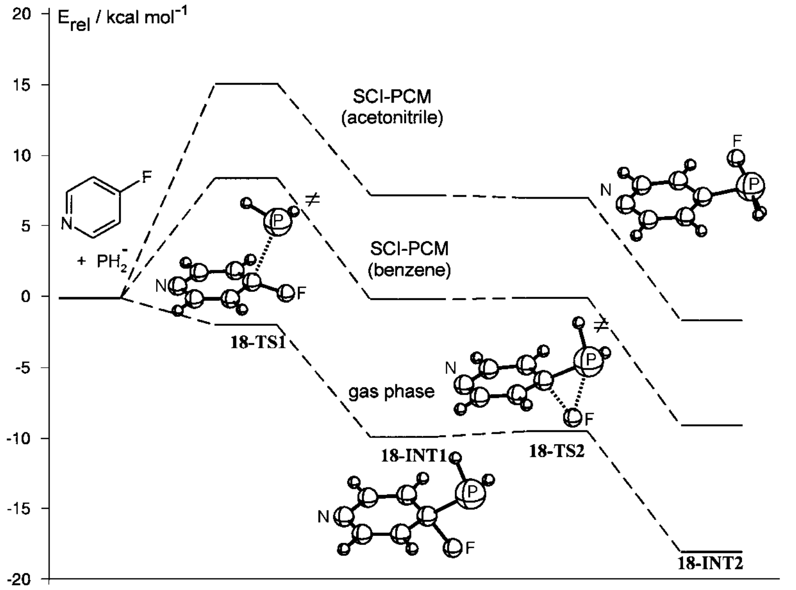


Figure 10. B3LYP/6-31G(d) energy profile for the model reaction of the phosphide anion with 4-fluoropyridine. The stationary points are optimised in the gas phase. SCI-PCM energies with acetonitrile and benzene as solvent are calculated with the gas phase geometries. Calculated lengths in Å: **18-TS1**: C_i–F 1.373, C_i–P 2.790. **18-INT1**: C_i–F 1.597, C_i–P 1.892. **18-TS2**: C_i–F 1.779, C_i–P 1.854, P–F 2.383. **18-INT2**: C_i–P 1.857, P–F 2.069. Energies are given in kcal mol^{-1}, relative to the separated reactants.

In benzene ($\varepsilon = 2.247$), the initial barrier of nucleophilic attack is lower (8.5 kcal mol^{-1}), as are the other relative energies compared with acetonitrile. In benzene, the elimination of fluoride from **18-INT2** would require 33.0 kcal mol^{-1}. This enthalpy difference implies an even higher activation barrier that is probably lowered by the silyl cation acting as an electrophile. In acetonitrile, the elimination is predicted to be less endothermic (+13.0 kcal mol^{-1}) and probably faster; this supports experimental findings.[16]

The formation of the Si–F bond is responsible for the overall exothermicity of the reaction, as can be deduced by comparing the enthalpies of the reactions of $H_3Si{-}PH_2$, PH_3 and PH_2^- with 4-fluoropyridine.

Our results indicate that, in the reaction of a nucleophilic phosphide anion with fluoroarenes, the rate-determining step in a polarisable solvent like acetonitrile is the formation of the C–P bond. This is in agreement with the results of a study of the nucleophilic substitution reaction of 2,4-dinitrochlorobenzenes with the thiomethoxide anion.[17] In less dipolar solvents like benzene, addition of PR_2^- is faster and elimination of the fluoride anion from a tetracoordinate fluoro-4-pyridylphosphanate $PyPH_2F^-$ is expected to be rate determining.

Summarising these results, a heterolytic dissociation of the silyl phosphane would explain a facile reaction of the reagent with fluoroarenes. However, an uncatalysed dissociation is not expected to occur either in the gas phase or in solution. Catalytic amounts of fluoride might generate the reactive PR_2^- anion. Although addition of CsF to the reaction mixture did not have an observable effect on the rate, this is no positive evidence for the absence of F^- catalysis. Fluoride, which originates from the polyfluorinated arenes, is expected to be present in catalytic amounts. Addition of more catalyst would then have no notable effect.

Alternatively, one might consider an intramolecular coordination of the silyl cation by an *ortho*-fluoro substituent. Experiments that address this suggestion will be performed in the near future.

Conclusion

A highly efficient synthesis has been established for polyfluoroarylphosphanes Ar_FPMe_2 by means of SiP or SnP cleavage reactions with polyfluoroarenes XC_6F_5, perfluorobiphenyl and perfluoropyridine. The one-pot synthesis of the phosphanes **1**–**7**, which uses a 1:1 mixture of the diphosphane P_2Me_4 and trimethylstannane Me_3SnH as reagent for the fluoroarene derivatives, is of particular value. This procedure can be transferred to various other combinations of element/element compounds, for example As_2Me_4, S_2R_2 or Se_2R_2 and Me_3SnH, for the preparation of the corresponding polyfluoroaryl derivatives Ar_FAsMe_2, Ar_FSR or Ar_FSeR.[18] In spite of extensive theoretical calculations on different levels, the pathway of the reaction could not be satisfactorily elucidated, because plausible transition states or intermediates led to unacceptably high energy barriers. So far, only a catalytically initiated predissociation of the silylphosphane to Me_3Si^+ and Me_2P^- could explain the observed facile substitution of fluorine by Me_2P. Therefore, additional experimental work will be necessary to come to a definite solution.

Experimental Section

General: Because of the air and moisture sensitivity of the $Me_3M'PMe_2$ compounds (M′ = Si, Sn) and the resulting polyfluoroarylphosphanes together with the possible toxicity, all experiments were carried out with high-vacuum and Schlenk techniques. The glassware used was thoroughly heated and evacuated. The NMR spectra were recorded on a Bruker AC200 spectrometer (^{1}H: 200.13 MHz, ^{19}F: 188.31 MHz, ^{31}P: 81.02 MHz). The NMR data are shown in Table 1. Mass spectra of the new compounds were obtained with a Varian MAT212 mass spectrometer. The fragmentation data are given together with the preparative procedure of the individual products. The X-ray structural analyses of the thiophosphanes **9**, **10**, **12**, **13** and **14** were performed on single crystals obtained from solutions in organic solvents. The data were collected with a STOE IPDS diffractometer ($Mo_{K\alpha}$ radiation), structure solution by direct methods (SHELXTL PLUS[19]) and structure refinement by SHELXL-97.[20]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-143856 (**9**), CCDC-143857 (**14**), CCDC-143858 (**10**), CCDC-143859 (**13**), CCDC-143860 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk. Crystal data, measurement conditions and results of the structure solutions are given in Table 4. The reagents $Me_3M'PMe_2$ (M′ = Si,[21] Sn,[22]) P_2Me_4[23] and Me_3SnH[24] were prepared according to literature methods.

Dimethyl(pentafluorophenyl)phosphane (1) and 1,4-bis-(dimethylphosphano)tetrafluorobenzene (6): Hexafluorobenzene (18 g, 100 mmol) and Me_3SiPMe_2 (0.55 g, 4 mmol) were condensed in an evacuated glass ampoule cooled with liquid nitrogen. The reactor was sealed and kept at 50 °C for 16 h. The volatile components (Me_3SiF and C_6F_6) were distilled off under argon by raising the bath temperature up to 120 °C, and **1** was obtained as a colourless liquid by vacuum distillation (0.1 mbar) over a bath temperature range of 20–50 °C (yield: 0.70 g, 75 %). Compound **6** (0.15 g, 7 %) was isolated from the residue as white crystals by sublimation in vacuo (0.1 mbar) by raising the bath temperature up to 100 °C. Characterisation of **6**: MS (70 eV, EI): *m/z* (%): 270 (100) [*M*]$^+$, 255 (37) [*M* – Me]$^+$, 223 (13) [*M* – Me – PH]$^+$, 208 (9) [*M* – 2Me – PH]$^+$; $C_{10}H_{12}F_4P_2$ (270.15).

Dimethyl(2,3,5,6-tetrafluorophenyl)phosphane (2): Pentafluorobenzene (1.85 g, 11 mmol) and Me_3SiPMe_2 (1.07 g, 8 mmol) were condensed in an evacuated glass ampoule cooled with liquid nitrogen. The reactor was sealed and kept at 70 °C for 10 h. The volatile components (Me_3SiF and C_6F_5H) were distilled off under argon by raising the bath temperature to 120 °C. Compound **2** (1.6 g, 95 %) was distilled off from the residue in vacuo (0.1 mbar) in form of a colourless liquid. MS (70 eV, EI): *m/z* (%): 210 (100) [*M*]$^+$, 195 (20) [*M* – Me]$^+$, 163 (72) [*M* – Me – PH]$^+$; $C_8H_7F_4P$ (210.11)

Dimethyl(4-chloro-2,3,5,6-tetrafluorophenyl)phosphane (3): A mixture of (pentafluoro)chlorobenzene (2.23 g, 11 mmol) and Me_3SiPMe_2 (1.07 g, 8 mmol) was kept at 50 °C for 5 h. Compound **3** (1.40 g, 82 %, with 94 % purity) was isolated in the form of a colourless liquid as described above for compound **2**. MS (70 eV, EI): *m/z* (%): 244 (100) [*M*]$^+$, 229 (67) [*M* – Me]$^+$, 227 (72) [*M* – Me – 2 H]$^+$, 197 (83) [*M* – Me – PH]$^+$; $C_8H_6ClF_4P$ (244.56).

Dimethyl(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)phosphane (4): Me_3SiPMe_2 (2.68 g, 20 mmol) was condensed in a reaction vessel, charged with perfluorotoluene (5.19 g, 22 mmol) and cooled with liquid nitrogen, in two equal portions. After the first portion was added and cooling was stopped, spontaneous heat liberation and boiling of Me_3SiF occurred. The mixture was kept at room temperature for 30 min, then cooled again and the second portion of the reagent was introduced to the reaction mixture by vacuum condensation. After the mixture was warmed up to room temperature and kept there for 2 h, the volatile components were distilled off under an argon atmosphere and compound **4** (4.37 g, 79 %) was distilled off as a colourless liquid in vacuo (0.2 mbar) over a bath temperature range of 30–50 °C. MS (70 eV, EI): *m/z* (%): 278 (100) [*M*]$^+$, 263 (11) [*M* – Me]$^+$, 261 (39)

0947-6539/00/0624-4619 $ 17.50+.50/0

Table 4. Crystal data, measurement conditions and results of structure solutions for compounds **9**, **10**, **12**–**14**.

	9	**10**	**12**	**13**	**14**
formula	$C_8H_7F_4PS$	$C_8H_6ClF_4PS$	$C_7H_6NF_4PS$	$C_{10}H_{12}F_4P_2S_2$	$C_{16}H_{12}F_8P_2S_2$
M_w [g mol^{-1}]	242.17	276.61	243.16	334.26	482.32
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pccn$	$P2_1/c$
a [Å]	9.166(2)	11.664(2)	9.316(2)	11.628(2)	9.879(2)
b [Å]	9.377(2)	10.189(2)	9.415(2)	12.200(2)	15.827(3)
c [Å]	11.975(2)	18.655(4)	11.589(2)	10.193(2)	12.519(3)
β [°]	100.27(3)	98.22(3)	97.19(3)		103.73(3)
V [Å^3]	1012.8(4)	2194.5(7)	1008.5(4)	1446.0(5)	1901.5(7)
Z	4	8	4	4	4
ρ_{calcd} [g cm^{-3}]	1.588	1.674	1.602	1.535	1.685
crystal size [mm^3]	0.16 × 0.12 × 0.08	0.80 × 0.16 × 0.08	0.20 × 0.16 × 0.12	0.32 × 0.20 × 0.16	0.40 × 0.16 × 0.16
μ [mm^{-1}]	0.49	0.70	0.50	0.61	0.52
2θ range [°]	8.72–52.02	10.68–56.33	10.60–56.24	10.62–56.36	10.38–56.62
range in hkl	±10, ±11, ±14	±15, ±13, ±24	±12, ±11, ±15	±15, ±16, ±13	±13, ±21, ±16
φ-scan [°]	199.5	200.4	199.5	200.6	200.2
$\Delta\varphi$ [°]	1.5	1.2	1.5	1.7	1.4
T [K]	213(2)	213(2)	213(2)	213(2)	213(2)
λ Mo$_{K\alpha}$ [Å]			($\lambda = 0.71073$)		
total reflections	7827	20759	9419	12835	18214
independent reflections	1867	5297	2369	1758	4538
reflections with [$I > 2\sigma(I)$]	1160	3739	1721	1444	3672
parameters	118	275	139	84	257
final R indices [$I > 2\sigma(I)$] $R1$	0.0554	0.0488	0.0574	0.0400	0.0441
$wR2$	0.1039	0.1128	0.1181	0.0896	0.1157
R indices (all data) $R1$	0.1040	0.0768	0.0864	0.0531	0.0564
$wR2$	0.1207	0.1274	0.1295	0.0968	0.1265
GooF	1.059	1.019	1.129	1.060	1.043
largest diff. peak/hole [e Å^{-3}]	0.252/–0.245	0.402/–0.456	0.288/–0.280	0.346/–0.326	0.356/–0.452

Weighting scheme: $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. $wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$. GooF $= [(\Sigma w (F_o^2 - F_c^2)^2)/(n-m)]^{1/2}$. Hydrogen atoms were included as fixed contributors in idealised positions

$[M-\text{Me}-2\text{H}]^+$, 259 (11) $[M-\text{F}]^+$, 244 (11) $[M-\text{F}-\text{Me}]^+$, 231 (46) $[M-\text{Me}-\text{PH}]^+$; $C_9H_6F_7P$ (278.11).

4-Dimethylphosphanotetrafluoropyridine (5): Me_3SiPMe_2 (1.34 g, 10 mmol) was condensed in four equal portions in a reactor charged with perfluoropyridine (1.86 g, 11 mmol) and cooled with liquid nitrogen. After each portion was added and cooling was stopped, heat liberation and ebullition of Me_3SiF were observed in the course of spontaneous warming-up. Then the mixture was worked up as described above for compound **4** to give compound **5** (1.82 g, 86%) as a colourless liquid. MS (70 eV, EI): m/z (%): 211 (100) $[M]^+$, 196 (12) $[M-\text{Me}]^+$, 165 (11) $[M-\text{Me}-\text{P}]^+$; $C_7H_6F_4NP$ (211.10).

4,4′-Bis(dimethylphosphano)octafluorobiphenyl (7): P_2Me_4 (0.239 g, 2.6 mmol) and $HSnMe_3$ (0.642 g, 3.9 mmol) were condensed in an evacuated Schlenk flask charged with decafluorobiphenyl (0.217 g, 0.65 mmol). The vessel was kept at 20 °C for 22 h and then at 90 °C for 20 min. The liquid components (Me_2PH and $HSnMe_3$) were distilled off in vacuo and the residue was sublimed in vacuo (0.05 mbar) at bath temperatures up to 100 °C to afford compound **7** (0.24 g, 88%) as white crystals. MS (70 eV, EI): m/z (%): 418 (100) $[M]^+$, 403 (4) $[M-\text{Me}]^+$, 388 (4) $[M-2\text{Me}]^+$, 371 (10) $[M-\text{Me}-\text{PH}]^+$; $C_{16}H_{12}F_8P_2$ (418.21).

Dimethyl(pentafluorophenyl)phosphane sulfide (8)

Method A: A mixture of dimethyl(pentafluorophenyl)phosphane (0.25 g, 1.1 mmol) and S_8 (0.048 g, 1.5 mmol) was heated at 90–100 °C for 1 h. After cooling to room temperature, traces of unreacted substrate were distilled off in vacuo (0.1 mbar) and the residue was dissolved in benzene (0.5 mL) and filtered. The resultant solution was diluted with pentane (ca. 5 mL) and cooled to –20 °C. The precipitated white crystals were filtered off, washed with pentane and dried in vacuo to give compound **8** (0.16 g, 56%). After evaporation of the solvents from the filtrate an additional quantity of crude product (0.08 g 27%) was obtained; this brought the total yield of **8** to close to 90%.

Method B: Hexafluorobenzene (23.3 g, 125 mmol), P_2Me_4 (0.42 g, 4.6 mmol) and $HSnMe_3$ (1.13 g, 6.9 mmol) were condensed in an evacuated glass ampoule cooled with liquid nitrogen. The ampoule was sealed under vacuum and kept at 20 °C for 48 h and then at 60 °C for 5 h. The precipitated Me_3SnF was filtered off and the volatile components (Me_2PH, $HSnMe_3$ and the main part of C_6F_6) were distilled off under argon. A mixture of the remaining C_6F_6 (ca. 2 mL) and compound **1** was then distilled off in vacuo (0.1 mbar) over a bath temperature range of 20–50 °C, collected in a Schlenk flask with S_8 (0.175 g, 5.47 mmol) and kept at 100 °C for 1 h. After the mixture was cooled to room temperature, the liquid components were distilled off in vacuo (0.1 mbar). The residue was then sublimed in vacuo (0.1 mbar) at bath temperatures up to 100 °C. Traces of typically smelling tin compounds were sublimed off in vacuo (0.1 mbar) at bath temperatures up to 40 °C to give compound **8** (0.69 g, 58%).

Dimethyl(2,3,5,6-tetrafluorophenyl)phosphane sulfide (9)

Method A: A mixture of compound **2** (1.83 g, 8.72 mmol), S_8 (0.336 g, 10.49 mmol) and benzene (2 mL) was heated at 100 °C for 45 min. After cooling the mixture to room temperature, the liquid components were distilled off in vacuo (0.1 mbar) and the residue was dissolved with warming in benzene (15 mL) and filtered. The resultant solution was concentrated by evaporation of the solvent (ca. 10 mL), diluted with pentane (5 mL) and cooled to –20 °C. The precipitated white crystals were filtered off, washed with pentane (3 mL) and dried in vacuo (0.1 mbar) at 40–50 °C for 1 h to afford compound **9** (2.06 g, 97%). MS (70 eV, EI): m/z (%): 242 (100) $[M]^+$, 227 (64) $[M-\text{Me}]^+$, 212 (9) $[M-2\text{Me}]^+$, 210 (10) $[M-\text{S}]^+$, 209 (23) $[M-\text{S}-\text{H}]^+$; elemental analysis calcd (%) for $C_8H_7F_4PS$ (242.18): C 39.68, H 2.91; found C 40.10, H 2.99.

Method B: Pentafluorobenzene (0.454 g, 2.7 mmol), Me_3SnPMe_2 (0.48 g, 2.14 mmol) and C_6D_6 (0.1 mL) were condensed in an evacuated NMR tube cooled with liquid nitrogen. The ampoule was sealed under vacuum and kept at 20 °C. The course of this reaction was monitored by ^{31}P NMR spectroscopy. After 22 h the yield of compound **2** reached 60%. Then the ampoule was kept for 2 h at 60 °C and the yield of compound **2** reached almost 92%. The reaction was completed after additional standing at 60 °C for 1 h. The liquid components (C_6D_6, C_6F_5H and **2**) were distilled off in vacuo (0.1 mbar) over a bath temperature range of 20–50 °C and collected in a Schlenk flask charged with S_8 (0.082 g, 2.57 mmol). The mixture was kept at 100 °C for 1 h and then cooled to room temperature. The liquid components were distilled off in vacuo (~0.1 mbar) and the residue was sublimed in vacuo (0.05 mbar) at bath temperatures up to 75°C. Traces of typically smelling tin compounds were sublimed off in vacuo (0.05 mbar) at a bath temperature of 40°C to afford compound **9** (0.33 g, 63%).

Dimethyl(4-chloro-2,3,5,6-tetrafluorophenyl)phosphane sulfide (10): A mixture of dimethyl(4-chloro-2,3,5,6-tetrafluorophenyl)phosphane (0.73 g, 3.9 mmol) and S_8 (0.12 g, 3.6 mmol) was kept at 95–100°C for 1 h. After cooling to room temperature, traces of substrate were distilled off in vacuo (0.1 mbar), and the residue was dissolved in pentane (ca. 25 mL) and filtered. The resultant solution was concentrated by evaporation of the solvent (15 mL) and cooled to −20°C. The precipitated white crystals were filtered off, washed with pentane and dried in vacuo to give compound **10** (0.52 g, 62%). MS (70 eV, EI): *m/z* (%): 276 (100) $[M]^+$, 261 (52) $[M-\mathrm{Me}]^+$, 246 (8) $[M-2\mathrm{Me}]^+$, 244 (8) $[M-\mathrm{S}]^+$, 243 (17) $[M-\mathrm{S}-\mathrm{H}]^+$; elemental analysis calcd (%) for $C_8H_6ClF_4PS$ (276.62): C 34.74, H 2.19; found C 34.21, H 2.31. After evaporation of the solvent from the filtrate, an additional amount of crude product (0.25 g, 30%) was obtained. This brought the total yield of compound **10** to almost 90%.

Dimethyl(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)phosphane sulfide (11): A mixture of dimethyl(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-phosphane (1.11 g, 4.0 mmol) and S_8 (0.15 g, 4.8 mmol) was kept at 80–90°C for 1 h. After cooling the mixture to room temperature, traces of substrate were distilled off in vacuo (0.1 mbar) and the residue was dissolved in benzene (5 mL) and filtered. The resultant solution was diluted with pentane (ca. 15 mL) and the precipitated white crystals were filtered off, washed with pentane and dried in vacuo to give compound **11** (0.81 g, 65%). MS (70 eV, EI): *m/z* (%): 310 (100) $[M]^+$, 295 (40) $[M-\mathrm{Me}]^+$, 278 (11) $[M-\mathrm{S}]^+$, 277 (16) $[M-\mathrm{S}-\mathrm{H}]^+$; elemental analysis calcd (%) for $C_9H_6F_7PS$ (310.18): C 34.85, H 1.95; found C 34.18, H 1.95. After evaporation of the solvents from the filtrate, additional 0.44 g (35%) of crude **11** were obtained; this raised the yield to almost 100%.

4-Dimethylthiophosphanotetrafluoropyridine (12): A mixture of 4-dimethylphosphanotetrafluoropyridine (0.88 g, 4.2 mmol) and S_8 (0.16 g, 5 mmol) was kept at 90–100°C for 1 h. After cooling to room temperature, traces of substrate were distilled off in vacuo (0.1 mbar) and the residue was dissolved in benzene (2 mL) and filtered. The resultant solution was diluted with pentane (ca. 5 mL) and the precipitated white crystals were filtered off, washed with pentane and dried in vacuo to give **12** (0.74 g, 73%). MS (70 eV, EI): *m/z* (%): 243 (100) $[M]^+$, 228 (27) $[M-\mathrm{Me}]^+$, 211 (6) $[M-\mathrm{S}]^+$, 210 (15) $[M-\mathrm{S}-\mathrm{H}]^+$; elemental analysis calcd (%) for $C_7H_6F_4NPS$ (243,16): C 34.58, H 2.49; found C 34.62, H 2.41. After evaporation of the solvents from the filtrate, additional 0.26 g (26%) of crude **12** were isolated, so that the total yield was close to 100%.

1,4-Bis(dimethylthiophosphano)tetrafluorobenzene (13): A mixture of hexafluorobenzene (0.37 g, 2 mmol) and Me_3SiPMe_2 (0.54 g, 4 mmol) was kept at 50–55°C for 15 h. The volatile components (Me_3SiF, C_6F_6, traces of reagent and **1**) were distilled off in vacuo (0.1 mbar) over a bath temperature range of 20–50°C. S_8 (0.16 g, 5 mmol) and C_6H_6 (ca. 5 mL) were added to the residue and the mixture was kept at 80°C for 1 h. After cooling the solution to 60°C, the yellow residue was dissolved in hot $CHCl_3$ (18 mL) and filtered through a thin layer of silica gel. The resultant solution was diluted with pentane (ca. 10 mL) and cooled to −20°C. The precipitated white crystals were filtered off, washed with pentane and dried in vacuo to give compound **13** (0.37 g, 68%). MS (70 eV, EI): *m/z* (%): 334 (100) $[M]^+$, 319 (25) $[M-\mathrm{Me}]^+$, 302 (20) $[M-\mathrm{S}]^+$, 287 (12) $[M-\mathrm{Me}-\mathrm{S}-\mathrm{H}]^+$, 270 (12) $[M-2\mathrm{S}]^+$; elemental analysis calcd (%) for $C_{10}H_{12}F_4P_2S_2$ (334.28): C 35.93, H 3.62; found C 36.21, H 3.58. After evaporation of the solvents from the filtrate, additional 0.12 g (22%) of crude **13** were isolated; this raised the total yield to close to 90%.

4,4′-Bis(dimethylthiophosphano)octafluorobiphenyl (14): A mixture of **7** (0.141 g, 0.337 mmol), S_8 (0.024 g, 0.749 mmol) and benzene (2 mL) was kept at 100°C for 1 h. After cooling the solution to about 75°C, hot benzene (12 mL) was added to the mixture and the resultant solution was filtered and cooled to 0°C. The precipitated white crystals were filtered off, washed with pentane and dried in vacuo to afford compound **14** (0.125 g, 77%). MS (70 eV, EI): *m/z* (%): 482 (100) $[M]^+$, 467 (27) $[M-\mathrm{Me}]^+$, 450 (15) $[M-\mathrm{S}]^+$; elemental analysis calcd (%) for $C_{16}H_{12}F_8P_2S_2$ (482.34): C 39.84, H 2.51; found C 39.72, H 2.53. After evaporation of the solvents from the filtrate, the resultant solid was dissolved in hot benzene (2 mL). The solution was cooled to 20°C, diluted with pentane (ca. 1.5 mL) and the precipitated white crystals were filtered off, washed with pentane and dried in vacuo to afford an additional quantity of the crude product (0.035 g, 21%); this brought the total yield of **14** to close to 100%.

Reaction of C_6H_5F with Me_3SiPMe_2: Me_3SiPMe_2 (0.059 g, 0.438 mmol), fluorobenzene (0.421 g, 4.38 mmol) and C_6D_6 (ca. 0.05 mL) were condensed in an evacuated NMR tube cooled with liquid nitrogen. The ampoule was sealed under vacuum, allowed to warm up to ambient temperature (17–20°C) and then kept at 180°C while periodically recording NMR spectra. The yield of dimethyl(phenyl)phosphane reached 19, 37 and 60% after 6.5, 29 and 90 h, respectively. ^{1}H NMR: $\delta = 7.5$ (m, 5H), 1.20 (d, $^2J(\mathrm{P,H}) = 3.2$ Hz, 6H);[15] ^{31}P NMR: $\delta = -47.11$ (s).

Reactions of C_6F_5H and C_6F_5Cl with Me_3SnPMe_2: Me_3SnPMe_2 (0.3 g, 1.3 mmol) and pentafluorobenzene (0.27 g, 1.6 mmol) or pentafluorochlorobenzene (0.32 g, 1.6 mmol) were condensed in an evacuated 5 mL ampoule cooled with liquid nitrogen. The ampoule was sealed, allowed to warm up to ambient temperature (20°C) and kept at this temperature for 16 h. It was then heated up to 60°C and held at this temperature for 2 h. The reaction mixture was cooled, Me_3SnF was filtered off as a white solid, and the solution was immediately transferred to a NMR tube. The solid was washed twice with C_6D_6 (ca. 0.3 mL) and the resulting solutions were added to the same tube. After sealing under vacuum, the NMR spectra were recorded. In the case of C_6F_5Cl the reaction mixture was also analysed by mass spectrometry, which showed the presence of all three isomeric derivatives $Me_2PC_6F_4Cl$ in accord with the NMR spectroscopy results.

Typical procedure for kinetic experiments: Me_3SiPMe_2 (0.13–0.42 g, 1–3 mmol), polyfluoroarene C_6F_5X (X = H, Cl, F or CF_3, 1.2–5.0 mmol) and, in some cases (see Figures 6–8), C_6D_6 (0.1–0.3 mL) and C_6H_6 (0.3–0.5 mL) were successively condensed in an evacuated NMR tube cooled with liquid nitrogen. The ampoule was sealed under vacuum, allowed to warm-up to ambient temperature (17–20°C) and then kept at the temperature of the kinetic measurement (see Figures 6–8) while periodically recording NMR spectra.

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