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Di- and Trifluorobenzenes in Reactions with Me_2EM (E = P, N; M = SiMe_3, SnMe_3, Li) Reagents: Evidence for a Concerted Mechanism of Aromatic Nucleophilic Substitution

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Dimethyl(trimethylsilyl)phosphane (Me₃SiPMe₂) has been successfully used for the substitution of fluorine variously in 1,3- (1) or 1,2-difluorobenzene (2) or in 1,3,5- (3) or 1,2,3trifluorobenzene (4) by the Me_2P group at 150–190 °C either in benzene solution or without solvent to give 1-(dimethylphosphanyl)-3-fluorobenzene (5) from 1, 1-(dimethylphosphanyl)-2-fluorobenzene (6) from 2, 1-(dimethylphosphanyl)-3,5-difluorobenzene (7) from 3 or a 1:1 mixture of 1-(dimethylphosphanyl)-2,3-difluorobenzene (8) and 1-(dimethylphosphanyl)-2,6-difluorobenzene (9) from 4. The substrate selectivities and regioselectivities exhibited by 4 with Me₃SiPMe₂ and in competitive reactions between 1 and 2 or 3 and 4 with Me₂PSiMe₃, Me₂PSnMe₃ or Me₂PLi indicate relative fluorine substituent rate factors $f_{o-F} > f_{m-F'}$ whereas for reactions that proceed through a two-step $S_{\!N}\!Ar$ mechanism the opposite sequence is typical. High-level quantum-chemical DFT and

Introduction

We recently reported that the compounds Me_2PM (M = SiMe₃, SnMe₃) are effective, convenient and versatile reagents for the substitution of fluorine atoms in polyfluoroarenes C₆F₅X (X = H, Cl, CF₃, PMe₂, AsMe₂) by a PMe₂ group in the position *para* to X.^[1,2] Mechanistically, these

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MP2 calculations predict that the gas-phase reactions should each proceed by a concerted mechanism with a single transition state. These predictions are in good agreement with the experimental observations, especially because the structural features of the Meisenheimer adduct are unfavourable for the S_N Ar mechanism. This proposal is consistent with the observation of the opposite sequence $(f_{m-F} > f_{o-F})$ for the reactions between the same substrates and MeONa in DMSO/ CH₃OH solvent mixtures. The novel phosphanes were characterized by spectroscopic (NMR) and spectrometric (MS) investigation, preparation of the thiophosphanes Ar_FPSMe₂ 10-12, their spectroscopic data and, in the case of 12, by its X-ray structure. The phosphanes 5-9 were treated with bis(benzonitrile)dichloropalladium(II) to afford the corresponding bis(phosphane)palladium dichloride complexes 17-21 and 23 in isolated yields of up to 95%.

reactions were considered to be comparable with those between polyfluoroarenes and oxygen, sulfur or nitrogen nucleophiles conventionally described in terms of the S_NAr mechanism. In a continuation of this approach, this paper reports on synthetic applications and experimentally observed substrate selectivities and regioselectivities, as well as on computational modelling of the mechanism, for the reactions between Me₂EM (E = P, N; M = SiMe₃, SnMe₃, Li) and the difluorobenzenes 1,3- (1) or 1,2-C₆F₂H₄ (2) or the trifluorobenzenes 1,3,5- (3) or 1,2,3-C₆F₃H₃ (4) . The potential to use the new Ar_FPMe_2 derivatives as ligands for transition metal complexes has been demonstrated by treatment with bis(benzonitrile)dichloropalladium(II).

Results and Discussion

Preparation of (Dimethylphosphanyl)fluorobenzenes Me₂PC₆ F_x H_{5-x} (x = 1, 2)

Dimethyl(trimethylsilyl)phosphane (Me_2PSiMe_3) was successfully used for substitution of fluorine by the Me_2P group in the precursors 1–4. Conditions and results are presented in Scheme 1. The reactions occur at temperatures be-





Scheme 1.

tween 170 and 190 °C either in benzene solution or in the absence of solvent to give (NMR spectroscopic data) the monosubstituted products 1-(dimethylphosphanyl)-3-fluorobenzene (5), 1-(dimethylphosphanyl)-2-fluorobenzene (6) or 1-(dimethylphosphanyl)-3,5-difluorobenzene (7) in yields between 40–70%. In the case of 4, a 1:1 mixture of 1-(dimethylphosphanyl)-2,3-difluorobenzene (8) and 1-(dimethylphosphanyl)-2,6-difluorobenzene (9) had previously been obtained.^[3a]

The (dimethylphosphanyl)difluorobenzenes 8 and 9 had also previously been prepared by treatment of 1-bromo-2,3and 1-bromo-2,6-difluorobenzene, respectively, with Me₂₋ PLi.^[3b] The phosphanes 5–9 were characterized by ¹H, ¹⁹F and ³¹P NMR spectroscopic investigations, by the preparation of the corresponding bis(phosphane)palladium dichloride complexes (Ar_FMe₂P)₂PdCl₂ 17–21 (Scheme 6, below) and also by the synthesis of the dimeric (phosphane)palladium dichloride complex [(1-Me₂P-3-FC₆H₄)PdCl₂]₂ (23) from phosphane 5 (Scheme 7, below). Compounds 5, 8 and 9 were also characterized in the form of their corresponding thiophosphanes $Ar_{\rm E}P(S)Me_2$ (10–12). The structure of 12 was determined by single-crystal X-ray diffraction studies [selected bond lengths and bond angles are collected in Table 5 (see below) and experimental and X-ray crystallographic data in Table 6; these data are similar to those for dimethyl(2,3,5,6-tetrafluorophenyl)phosphane sulfide^[1]]. The spectroscopic and analytic data for compounds 5-7 and 10 are given in the Exp. Section; those for compounds 8, 9, 11 and 12 have already been published.^[3]

Substrate Selectivities and Regioselectivities of Reactions between Di- or Trifluorobenzenes and Me₂PM (M = SiMe₃, SnMe₃, Li)

The difluorobenzenes 1 and 2 and the trifluorobenzenes 3 and 4 react with Me_2PSiMe_3 markedly less readily than pentafluorobenzenes C_6F_5X . Compounds 3 and 4 display reasonable reaction rates only at 150 °C and 1 and 2 only

at 170 °C, rather than at 20–70 °C for pentafluorobenzenes C_6F_5X .^[1,2] However, the di- and trifluorobenzenes are significantly more reactive than C_6H_5F , for which temperatures above 180 °C are necessary.^[1]

The relative substrate reactivities with Me₂PM (M = SiMe₃, SnMe₃) – 2 > 1 and 4 > 3 – were determined through the competitive reactions shown in Scheme 2 and Scheme 3, respectively. The product distributions observed for the Me₂PM (M = SiMe₃, SnMe₃) reagents in benzene or cyclohexane indicate relative rate factors $f_{o-F} > f_{m-F}$ in competitions between 2 and 1, and between 4 and 3 and in terms of the regioselectivity in the case of 4. In the more polar solvent CH₃CN the relative substrate reactivities and regioselectivities for the latter competition experiment decrease, but are still in favour of position 2.

	1 + 1 :	2 - 1	Me ₂ PEMe ₃ 170 °C solv.	5	+	6
E = Si	solv	$C = C_6 D_6$	13 h	1	:	3.4
	solv.	$= C_6 H_{12}$	15 h	1	:	3.9
			30 h	1	:	4.4
E = Sn	solv.	$= C_6 H_{12}$	12 h	1	:	4.1

Scheme 2.

If Me₂PLi is used instead of Me₂PM (M = SiMe₃, SnMe₃) in C₆D₆ solution, the f_{o-F}/f_{m-F} ratio remains nearly the same (Scheme 3). Obviously because of the higher polarity of the P–Li bond in relation to the P–Si and P–Sn bonds, the reaction is in this case already complete within 0.5 h at temperatures between 5 and 20 °C.

These data establish the general sequence $f_{o-F} > f_{m-F}$, whereas for the same substrates with MeONa in DMSO/ CH₃OH the inverse correlation $f_{m-F} > f_{o-F}$ was obtained (e.g., the ratio 1-MeO-2,3-F₂C₆H₃/1-MeO-2,6-F₂C₆H₃ = 4:1 in the reaction of **4**).^[4] This reaction with an anionic nucleophile in a polar solvent thus shows greater activities

	3 + 4 — 1 : 1	solv.	7	+	8	+	9
	M = SiMe ₃ , SnM M = Li 0-20 °C	Me ₃ 150 C	°C				
(a) $M = SiMe_3$	solv. = C_6D_6	15 h	1	:	1.7	:	2.0
	solv. = C_6H_{12}	15 h	1	:	2.2	:	2.7
		30 h	1	:	2.2	:	2.5
$M = SnMe_3$	solv. = C_6H_{12}	15 h	1	:	2.5	:	3.1
(b) $M = SiMe_3$	solv. = CH_3CN	3 h	1	:	1.6	:	1.5
(?) M = Li	solv. = C_6D_6	0.5 h	1	:	4.1	:	5.0

Scheme 3.

of substrates with mutual *meta* fluorine substituents than in the isomers with adjacent fluorine atoms, so the data obtained for the Me_2PM reagents apparently suggest a fluorine effect different from those seen in S_NAr -type reactions.

These results also show that the observed selectivities are qualitatively independent of the leaving group M in the Me_2PM reagent. However, the effect of the nucleophilic centre could be very significant. To test this possibility we studied the reactions of **3** and **4** with (dimethylamino)trimethylsilane (Me_2NSiMe_3).

Reactions of 3 and 4 with Me₃SiNMe₂

The reactions of 3 and 4 with Me_3SiNMe_2 were carried out in sealed ampoules. Conditions and results are presented in Schemes 4 and 5.



Scheme 4.



Scheme 5.

Both **3** and **4** react with Me₃SiNMe₂ less readily than with the phosphane nucleophiles in Scheme 2, analogously to pentafluorobenzene and its C₆F₅X derivatives.^[2] The relative proportions of the products **13–15** were estimated from the integrals of the ¹⁹F NMR signals (see Exp. Sect.). The substrate **3** with *meta* fluorine atoms showed a higher reactivity with Me₂NSiMe₃ than its isomer **4**. In **4** the 1and 3-CF units exhibit the highest electrophilicity, consistently with fluorine partial rate factors $f_{m-F} > f_{o-F}$. This is in contrast with the relative substrate selectivities and regio-selectivities observed for the phosphanyl-defluorinations (Schemes 2 and 3), but analogous to the results observed for the reactions of **3** and **4** or **1** and **2** with sodium methoxide.

The reactions with sodium methoxide (MeONa) had previously been assumed to proceed through a S_NAr mechanism. Correspondingly, the generally observed *para < ortho* < *meta* sequence for the fluorine substituent effect on the rates of nucleophilic fluorine substitution in polyfluoroarenes would be explained by Meisenheimer-adduct-like transition states (TSs) with the ring a π -electron anionic pentadienyl unit and increased electron density in the 1-, 3- and 5-positions.^[5] The fluorine substituents ortho and para to the site of nucleophile attack in the fluoroarene substrate therefore exert a destabilizing p,π -repulsion effect in the TS, which is overcompensated for the ortho-fluorine atom by its electron-withdrawing inductive effect.^[6] In these terms, the substrate reactivity correlations 2 < 1 and 4 < 3 could be expected, as well as the predominant F-1 replacement in 4, consistently with the *ortho*-F < meta-F activating effect. As shown above, this relation was indeed observed for the nitrogen reagent Me₂NSiMe₃, whereas the opposite *meta* <ortho sequence was found for the phosphorus reagents Me_2PM (M = SiMe_3 or SnMe_3).

Quantum-Chemical Calculations and Discussion of the Mechanism

Quantum-chemical calculations were carried out for the reactions between fluorobenzene or 1,2,3-trifluorobenzene (4) and Me₂ESiMe₃ (E = P or N), including the TSs, in order to elucidate the mechanistic features responsible for the observed reactivity, with application of the DFT method B3LYP and the basis sets 6-31+G(d,p) and 6-311++G(2d,p) for geometry optimizations as implemented into the program package GAUSSIAN $03.^{[7]}$ For energy determinations Grimme's recently developed SCS-MP2 method [SCS-MP2/6-31+G(d,p)//B3LYP/6-31+G(d,p)] was

Table 1. Relative energies, with respect to the sum of the energies of the starting materials, calculated by DFT [B3LYP/6-31+G(d,p)]/B3LYP/6-31+G(d,p)] and SCS-MP2 $\{6-31+D(d,p)//B3LYP/6-31+G(d,p) [kcalmol^{-1}]\}$.

Reacting system	Method	TS	E (sum of products)
Fluorobenzene +	DFT	36.55	-41.00
Me ₂ PSiMe ₃	SCS-MP2	30.26	-49.13
Fluorobenzene +	DFT	47.35	-31.21
Me ₂ NSiMe ₃	SCS-MP2	34.30	-33.05
4 (position 1) +	DFT	30.56	-46.74
Me ₂ PSiMe ₃	SCS-MP2	23.63	-55.30
4 (position 2) +	DFT	27.88	-49.12
Me ₂ PSiMe ₃	SCS-MP2	19.79	-57.98
4 (position 1) +	DFT	43.96	-35.29
Me ₂ NSiMe ₃	SCS-MP2	29.26	-39.29
4 (position 2) +	DFT	42.84	-34.69
Me ₂ NSiMe ₃	SCS-MP2	28.94	-38.06

used.^[8] All stationary points were subjected to frequency analyses. Furthermore, the geometries obtained for the transition states were used for IRC calculations in order to ensure the correct trajectories between starting materials, transition states and products. The data reported refer to 0 K and include DFT zero-point energies. The calculated relative energies, referenced to the sums of the energies (*E*) of the corresponding substrates and nucleophiles ($E_{rel} =$ 0.00 kcalmol⁻¹), are presented in Table 1.

The Reaction Course

From the optimizations and from the IRC calculations for the reactions of fluorobenzene and **4** with the neutral nucleophiles Me₂ESiMe₃, similar energy profiles, each with one transition state and two minima corresponding to "loose" or van der Waals complexes (vWces) formed by the starting components (starting vWc) and by the products (final vWc), respectively, are obtained in all cases.^[9] There is no indication of Meisenheimer-adduct-like intermediates. The single TSs correspond to the simultaneous formation of the C–E bond and cleavage of the C–F and Si–E bonds (see Table 1, Figures 1 and 2).



Figure 1. Schematic energy profile for the reaction between fluorobenzene and Me_2PSiMe_3 [SCS-MP2/6-31+G(d,p)//B3LYP/6-31+G(d,p)].

Thus, according to the calculations, the reactions of these neutral nucleophiles with fluorobenzenes involving a Me_3Si -assisted substitution of the relatively weak leaving group fluoride, as studied here, are concerted processes, leading to the Me_2E -substituted aryl compounds with Me_3 -SiF as the second product.

An aromatic nucleophilic substitution mechanism of such a type, involving a single TS (A_ND_N mechanism^[10]), had previously been reported by Williams et al. for the transfer of 1,3,5-triazinyl groups from aryloxide ligands to an anionic aryloxide or to amine and pyridine nucleophiles^[10b,10c] and from a pyridinium ligand to amine or hydroxide nucleophiles^[10d] in aqueous solution. These reactions obey linear log k_{nuc} versus nucleophile p K_a relationships. By the same reasoning, this mechanism was also suggested for the replacement of a pentafluorophenoxy group by a fluoride anion in 2,3,5,6-tetrafluoro-4-(pentafluorophenoxy)pyridine.^[11] In the opinion of the authors of ref.^[10b] this mechanism is based on the weak basicities both of the entering and of the leaving ligands. However, the ability of the transferred group, particularly of 1,3,5-triazinyl, to allow efficient negative charge dispersion favours the two-step S_NAr mechanism with a discrete Meisenheimeradduct-like intermediate.[12-14] This conclusion is supported by the observation of Meisenheimer complexes formed by nitroarenes in the gas phase.^[15] It is of fundamental importance that neither high basicity of an entering or leaving ligand nor efficient resonance stabilization of a negative π charge in a ring are present in the compounds of our study. These properties are unfavourable for the S_NAr mechanism, thus strongly supporting the A_ND_N mechanism.

In our opinion, based on the calculations, another principal reason for the observed reaction (i.e., to escape the S_NAr mechanism) is the disfavouring of the Meisenheimer adduct in the gas phase, due to charge separation. One may argue that the concerted A_ND_N mechanism of the studied reactions should reduce the charge separation in the TS in relation to the S_NAr mechanism.

From this point of view, the mechanism involving a Meisenheimer intermediate could seem to be especially favourable for reactions with anionic nucleophiles, because in this case the formation of adducts should be accompanied by negative charge delocalization. To check this assumption



Figure 2. TS geometries for the reactions between: a) compound 4 (position 1) and Me₂PSiMe₃, b) compound 4 (position 2) and Me₂P-SiMe₃, c) compound 4 (position 1) and Me₂NSiMe₃, d) compound 4 (position 2) and Me₂NSiMe₃, and e) fluorobenzene and Me₂NSiMe₃, calculated at the B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level.



the anionic intermediate 16, resulting from attack of the methoxide ion at the 2-position of 4, was included in the computational study. Surprisingly, in 16 (Figure 3), which corresponds to a shallow local minimum, the C²-F bond is enormously stretched (1.58 Å), whereas the C²-O bond is of normal length (1.43 Å). Moreover, the calculations predict an extreme kinetic instability of this adduct, with only a symbolic energy barrier of 1.3 kcalmol⁻¹ to the escape of the fluoride to form a complex of 2,6-difluoroanisole and F^{-} (-42.8 kcalmol⁻¹ better in energy than the sum of 4 and OCH_3^{-}), whereas ca. 17 kca1mol⁻¹ would be needed to stretch the C-OCH₃ bond up to a length of 2.4 Å. Thus, even in this special case the intermediate should be considered an elusive gas-phase complex of the substitution product with a fluoride anion rather than a Meisenheimer adduct.

Figure 3. Calculated structure of intermediate **16** for the reaction between compound **4** (position 2) and the methoxide ion [B3LYP/6-311++G(2d,p)].

Similarly, the gas-phase calculations for anionic Meisenheimer intermediates formed from fluorobenzene or 4 (positions 1 and 2) and the fluoride anion (Table 2) also result in local minima on the energy surface corresponding to intermediates of quite low thermodynamic stability [-7.5 kcalmol⁻¹ in the case of fluorobenzene and -16 to -18 kcalmol⁻¹ for the complexes of **4** at the SCS-MP2-6-311++G(2d,p) level, relative to the sums of the starting materials]. Even in the cases of the fluorobenzene Meisenheimer intermediate and that of 4 it requires only about 2–4 kcalmol⁻¹ to stretch one of the C–F bonds to 2.4 Å. In each case the global minimum corresponds to a hydrogenbonded complex with the fluoride ion situated at the parahydrogen atom of the aromatic ring (ca. $10-12 \text{ kcal mol}^{-1}$ lower in energy than the Meisenheimer adduct). One may argue that there are two main reasons for the calculated intermediacy of these special Meisenheimer adducts. The first is the capability to distribute the negative charge over the ring system. The second is the enhanced stability of a CF₂ moiety. Thus, whereas a Meisenheimer adduct with a halogen atom at the sp³ carbon is in general an elusive halogen substitution intermediate, it has been possible to observe a *gem*-difluoro Meisenheimer complex formed by picryl fluoride and a fluoride anion by NMR spectroscopy.^[16]

In general, these results obviously indicate that a Meisenheimer adduct intermediate with no strongly electronwithdrawing groups and, moreover, formed by a neutral nucleophile is inherently disfavoured in the gas phase and probably also in nonpolar media.

Reaction Energetics, TS Structures, Substrate Selectivities and Regioselectivities

The data in Table 1 demonstrate that the experimentally observed relative substrate selectivities and regioselectivities qualitatively correspond to the calculated reaction energies for an A_ND_N mechanism. Because the reactions were carried out in essentially nonpolar media, the calculations performed for the gas phase seem to be fairly suitable to the experimental conditions. From the calculated heats of reaction (sums of energies of products) and activation barriers one can derive that fluorobenzene is less reactive than 4 towards both nucleophiles. Both Me₂ESiMe₃ compounds (E = P, N) kinetically prefer the C² position of 4, by ca. 3 and 1 kcalmol⁻¹, respectively, whereas thermodynamically this position is more attractive only for Me₂PSiMe₃, because for Me₂NSiMe₃ a slightly smaller exothermicity for attack at C² is calculated.

From the structural features of the stationary points of the calculated reaction path we conclude that the ring obviously maintains a considerable degree of benzenoid resonance.^[10] This is clearly seen by comparison of the geometric parameters of the ring skeleton of fluorobenzene or 4 with the TSs in their reactions with Me₂ESiMe₃ on the one hand, and with the Meisenheimer adducts of fluorobenzene and 4 with the fluoride anion on the other. Thus, the calculated C–C bond lengths in 4 amount to $C^1-C^2 = C^2-C^3 =$ 1.3974 Å, $C^3-C^4 = C^1-C^6 = 1.3897$ Å, and $C^4-C^5 = C^5-C^6$ = 1.3939 Å. The corresponding parameters for the Meisenheimer adducts are presented in Table 2. In the (asymmetric) TS for the reaction between 4 and Me₂PSiMe₃ slightly elongated C^1 - C^2 and C^2 - C^3 bonds (1.4274 and 1.4280 Å), slightly shortened C^3-C^4 , C^6-C^1 bonds (1.3827) and 1.3801 Å) and again slightly shortened C^4-C^5 , C^5-C^6 bonds (1.4000 and 1.4011 Å) are found. This TS geometry is intermediate between those of the substrate and the Meisenheimer adducts, thus indicating significant aromatic character in this TS.

Table 2. Calculated energies and geometrical parameters of the Meisenheimer adducts formed by fluorobenzene and 4 with F^- [the atom numbers correspond to those of the substrates; SCS-MP2/6-311++G(2d,p)//B3LYP/6-311++G(2d,p)].

Substrate	Energy ^[a]				Inter	Interatomic distances [Å]				
		C^1-F	C ² –F	C ³ –F	C^1 – C^2	$C^{2}-C^{3}$	$C^{3}-C^{4}$	$C^{4}-C^{5}$	C ⁵ -C ⁶	$C^{1}-C^{6}$
Fluorobenzene 4 (position 1) 4 (position 2)	-7.47 -17.71 -15.94	1.482 1.468 1.380	1.370 1.468	1.371 1.380	1.444 1.443 1.441	1.380 1.369 1.440	1.402 1.394 1.371	1.402 1.400 1.400	1.380 1.380 1.400	1.444 1.446 1.371

[a] kcalmol⁻¹ relative to sum of substrate + F⁻.

In our opinion the preservation of substantial aromaticity in the A_ND_N mechanism TSs provides a good basis for a qualitative explanation of the substrate selectivities and the regioselectivity of 4 in favour of a preferred attack at the 2-position in the reactions under investigation. Firstly, this diminishes the destabilizing p,π -repulsion effect of ortho-F relative to a Meisenheimer-adduct-like TS. At the same time, the more electron-deficient the carbon atom of a reaction centre is as a result of the combined fluorine substituents' inductive effects, the more stable the respective TS will be. This is in favour of an enhanced reactivity of 2 in relation to 1 and of 4 in relation to 3. The same holds for position C^2 in 4, centred between two CF groups, in relation to position C^1 . Secondly, because of the formation of a three-dimensional tetrahedral environment around the reacting carbon centre in the TS, unfavourable interactions of the neighbouring CF units in 2 and 4 are strongly diminished. In the latter case this effect is more significant for C² with the two remaining CF units at favourable 1,3-distances whereas for attack at C¹ the two CF units remain at unfavourable 1,2-distances. These substituent effects are accompanied by measurements showing that ortho-difluorobenzene is higher in energy than its meta isomer by ca. 3.5 kcalmol⁻¹ at 25–200 $^{\circ}C^{[17]}$ and with the results of our calculations (SCS-MP2) revealing that 1,2,3-trifluorobenzene is significantly (7.7 kcalmol⁻¹) destabilized in relation to 1,3,5-trifluorobenzene.

Effects of the Natures of Nucleophilic E-Centres

All the reactivity differences discussed for the reactions of Me₂PSiMe₃ are less pronounced for those of Me₂N-SiMe₃, because here the calculated results predict similar relative reactivities of fluorobenzene and 4 and a very small reactivity difference between the 1- and 2-positions of 4. Consequently, fluorine substitution at the 1-position should be statistically predominant, as is observed experimentally (with some small discrepancies, possibly caused by solvent effects, between the calculated and experimentally observed replacement rates). Moreover, according to the calculations, the formation of the Me₂N product 13 is thermodynamically favoured, whereas 14 is kinetically preferred (Table 1). This may be attributed to the fact that the Me₂P products 8 and 9 each prefer a conformation with a Me₂P-position quasi-perpendicular to the benzene ring (Figure 4). In contrast, the anilines 13 and 14, as would be expected, prefer

conjugation between the dimethylamino group and the benzene system, with 2,6-difluorodimethylaniline obviously being more sterically hindered than 2,3-difluorodimethylaniline.

In view of these arguments, the calculated internuclear distances in the TS structures (Table 3, Figure 5) are of particular interest. In the TSs for the Me₂PSiMe₃ reactions the C–F and C–E contacts are less stretched (only by 12–18%) than those of the reactions with Me_2NSiMe_3 (by 18–25%) relative to standard bond lengths (C-F 1.35 Å, C-P 1.84 Å, C-N 1.47 Å, Ph-N 1.42 Å).^[18] This means that the phosphorus reagent in the TS approaches the benzene skeleton more closely and that the C-F bond is less stretched than in the case of the nitrogen reagent. On the other hand, the Si-F contacts in the TS with the nitrogen nucleophile are much shorter than in that of the phosphorus one, in the former case being noticeably below the sum of the van der Waals radii of Si and F (3.5–3.6 Å). A loose Si–F coordination can therefore be assumed in the TS with Me₂NSiMe₃. In contrast, in the TS with the phosphorus reagent the Si-F distance is not smaller than the sum of van der Waals radii, so the Me₃SiF molecule is formed at the very end of the reaction course. Reaction path calculations indicate that the leaving fluoride ion moves along the Me₂PSi subunit with a rather short P-F distance (no minimum, however).

Table 3. Calculated geometrical parameters of TSs formed by fluorobenzene and 4 with Me_2ESiMe_3 [B3LYP/6-31+G(d,p)].

Substrate	Me ₂ ESiMe ₃	Internue	elear dista	ances in t	he TSs[Å]
		E–C	C–F	E–Si	Si–F
Fluorobenzene	·	2.057	1.552	2.305	3.485
4 (position 1)	Me ₂ PSiMe ₃	2.083	1.518	2.307	3.486
4 (position 2)		2.077	1.524	2.310	3.438
Fluorobenzene		1.706	1.640	1.910	2.574
4 (position 1)	Me ₂ NSiMe ₃	1.686	1.607	1.933	2.566
4 (position 2)		1.681	1.621	1.933	2.505

These properties can probably be attributed to the differences in the energies and lengths of the C–N and C–P bonds. Obviously, because of the larger C–N bond energy, relative to the C–P bond, a smaller degree of C–N bond formation is necessary in order to compensate for the energy expenses of the C–F bond stretching and the out-ofplane deviation in the TS of the reaction with Me₂NSiMe₃, relative to the C–P bond formation in the TS of the reaction with Me₂PSiMe₃. Therefore, the greater C–F bond stretch-



Figure 4. Calculated structures of **8**, **9**, **13** and **14** [B3LYP/6-3 l+G(d,p)//B3LYP/6-31+G(d,p)].





Figure 5. Calculated structures of complexes and TS for the reaction between 4 (position 2) and Me₂PLi.

ing and shorter E–Si distance in the nitrogen TS allow a closer Si—F approach and a stronger Si–F linkage than in the TS with the phosphorus reagent.

Interestingly, for both Me₂ESiMe₃ reagents the TSs of the reactions with fluorobenzene correspond to a less pronounced synchronism of the process than those of the reactions with 4. In the fluorobenzene TS some imbalance between bond formation and bond fission is observed: the C-F contact is stretched to a greater degree (by ca. 18% for E = P and by ca. 25% for E = N with respect to the standard bond lengths) in relation to the C-E contacts (by ca. 12% for E = P and by ca. 20% for E = N). On the other hand, the stretchings of both C-F and C-E bonds in the TS of 4 are nearly balanced (ca. 12–13% for E = P and ca. 18–20% for E = N). In terms of the More O'Ferral–Jencks diagrams,^[19] all TSs related to 4 are obviously positioned near the tightness diagonal, the phosphorus TSs being somewhat more shifted toward the top-left (Meisenheimer adduct) corner than the nitrogen TSs (presuming very similar curvatures of the energy surfaces for all these reactions along the reaction coordinate). Relative to these TSs, the TSs involving fluorobenzene deviate somewhat from the tightness diagonal toward the top-right (products) corner. This corresponds to somewhat "later" TSs in reactions of fluorobenzene than in the case of those of 4, consistently with the reactivity correlation of these substrates.

Me₂PLi as a Model Anionic Nucleophile

As specified above, the reactions between di- or trifluorobenzenes and Me_2PLi exhibit the same substrate selectivities and regioselectivities as their reactions with the Me_2PM (M = SiMe₃, SnMe₃) reagents. The same concerted A_ND_N mechanism can therefore also be assumed for this case. Because of the nonpolar character of the medium, Me_2PLi is subject to a strong ionic association and can obviously be approximated as reacting in form of a tight ion pair. As a consequence, the essential prerequisite for the S_NAr mechanism – the charge separation in the Meisenheimer adduct and in the Meisenheimer adduct-like TS – is not fulfilled, whereas in the A_ND_N TS the incipient fluoride anion will be stabilized by coordination to the lithium cation. To check these expectations we performed SCS-MP2/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations for the reaction between 4 (2-position) and Me₂PLi. As anticipated, Me₂PLi forms a rather strong Lewis acid/base complex with 4 (calculated coordination energy ca. 15 kcalmol⁻¹). The reaction is calculated to proceed through a concerted $A_N D_N$ mechanism, leading in the gas phase to a strongly bound LiF–(2,6-difluorophenyl)dimethylphosphane complex (ca. 20 kcalmol⁻¹ lower in energy than the sum of the products). The calculated structure of the TS is depicted in Figure 5; its calculated relative energy (the energy of the starting vWc is taken as reference; $E_{rel} = 0.0$ kcalmol⁻¹) and geometry parameters are presented in Table 4.

Table 4. Calculated relative energies and interatomic distances of the complexes and TS for the reaction between compound 4 (position 2) and Me₂PLi [SCS-MP2/6-311++G(2d,p)//B3LYP/6-311++G(2d,p)] relative to the sum of the energies of Me₂PLi and 4.

	Energy	Interatomic distances [Å]					
	[kcal mol ⁻¹]	Li–P	Li–F ¹	Li–F ²	$C^2 - P$	$C\!\!-\!\!F^1$	C–F ²
Starting complex	-30.90	2.35	2.07	2.10		1.36	1.36
TS Final complex ^[a]	-24.80 -105.98	2.33 2.56	2.04 2.05	1.92 1.62	2.95 1.86		1.43

[a] Sum of the energies of the products: -88.44 kcalmol⁻¹.

These data show that in the TS neither the Li–P nor the Li–F¹ contact are markedly stretched in relation to the starting complex; however, considerable changes are observed in the approach of the Me₂P group to C², leading to a C²–P contact of 2.97 Å, much longer than in the TS for the Me₂PSiMe₃ nucleophile. Dramatic changes accompany the generation of the final complex, with practically the standard value (1.85 Å) for the C²–P bond and a very short Li–F² bond (1.61 Å). Together with an extremely low activation energy and high exothermicity of the reaction, these results are the characteristic features of an early (reagent-like) TS, so one can conclude that the transformation of the benzene ring into the anionic cyclohexadienyl system is also energetically unfavourable in this case and that the principal

stabilizing interactions in the TS are the Li···P and Li···F coordinations (Li– F^2 1.93 Å is close to the average between those in the starting and final complexes).

Preparation of Fluorinated (Dimethylphenylphosphane) palladium Dichlorides

The application of the fluorinated dimethylphenylphosphanes Ar_FMe_2P for the preparation of transition metal complexes has been demonstrated by the syntheses of the palladium complexes **17–22** in 71–95% isolated yields as shown in Scheme 6. The reactions were carried out as reported for the ligand Ph₂PCH=CH₂.^[20a]

2	Ar _F PMe ₂ +	trans-[(Ph	CN)2PdCl2]	-2PhCN	(Ar _F PMe ₂) ₂ F	PdCl ₂
				C ₆ H ₆ , 20 °C, 1–2 h	17–22	
Ar _F =	3-FC ₆ H ₄ 17 , 83 %	2-FC ₆ H ₄ 18, 95 %	3,5-F ₂ C ₆ H ₃ 19 , 88 %	2,3-F ₂ C ₆ H ₃ 20 , 87 %	2,6-F ₂ C ₆ H ₃ 21 , 71 %;	4-CF ₃ C ₆ F, 22 , 88 %

Scheme 6.

The structures of 17-22 were assigned on the basis of their ¹H, ¹⁹F and ³¹P NMR and elemental analysis data and those of compounds 18, 19, 21 and 22 were also supported by single-crystal X-ray diffraction studies (see Figures 6, 7, 8, and 9; selected bond lengths and bond angles are collected in Table 5 and experimental and X-ray crystallographic data in Table 6). In addition, the molecular geometries in the solid state were determined by far-infrared (FIR) spectroscopy (Exp. Section). The presence of three v_{Pd-Cl} valence bands in the spectra of 18 and 19, and probably also those of 17 and 21, indicate the formation of cis and *trans* isomer mixtures.^[20] The presence of two v_{Pd-Cl} bands in the spectra of 20 and 22 indicates the trans configuration. The X-ray analysis of randomly selected crystals characterized 18 and 22 as their trans isomers and 19 as a cis isomer. Because the complexes 17-21 each exhibit two signals in their ³¹P{¹H} NMR spectra (see Exp. Section), they obviously exist in CDCl₃ solution as mixtures of cis and trans isomers. Compound 22 shows only one singlet resonance, which can be ascribed to the trans isomer.



Figure 6. X-ray structure of 18.





Figure 7. X-ray structure of 19.



Figure 8. X-ray structure of 21.



Figure 9. X-ray structure of 22.

The reaction between *trans*-[(PhCN)₂PdCl₂] and **5** (ratio 1:1) was carried out under conditions (Scheme 7) similar to those of Scheme 6 and led to the binuclear complex **23** in 83% yield. The structure of **23** [di- μ -chloro-dichlorobis{(3-fluorophenyl)dimethylphosphane}dipalladium(II)] was assigned on the basis of its ¹H, ¹⁹F and ³¹P NMR, X-ray (Figure 10) and elemental analysis data.

Conclusions

Dimethyl(trimethylsilyl)phosphane (Me_3SiPMe_2) has been shown to act as a convenient and effective reagent for dimethylphosphanyl-defluorination reactions of the relatively weakly electrophilic di- and trifluorobenzenes. The



Table 5. Selected bond lengths [pm] and angles [°] in compounds 12, 18, 19 and 21–23.

E-C bonds	12 ^[a]	18 ^[a]	19	21	22 ^[a]	23
Pd–E bonds		Pd(1)-P(1): 232.63(4)	Pd(1)-P(1): 225.9(2)	Pd(1)-P(1): 226.23(9)	Pd(1)-P(1): 230.73(17)	Pd(1)–P(1): 221.47(11)
bolids		Pd(1)-P(1)#1: 232.63(4)	Pd(1)-P(2): 225.42(19)	Pd(1)-P(2): 226.48(10)	Pd(1)–Cl(1): 229.29(15)	Pd(1)–Cl(1): 228.99(10)
		Pd(1)-Cl(1): 230.60(5)	Pd(1)-Cl(1): 235.63(19)	Pd(1)-Cl(1): 234.40(9)		Pd(1)–Cl(2): 246.70(12)
		Pd(1)-Cl(1)#1:	Pd(1)-Cl(2):	Pd(1)-Cl(2):		Pd(1)–Cl(3):
P-C	$P(1) = C(1) \cdot 1804(2)$	230.60(5) P(1)-C(1): 181.88(17)	236.68(18) P(1)-C(1): 180.8(7)	235.45(10) P(1)=C(1): 181.9(3)	P(1)-C(1): 181 5(6)	233.36(10) P(1)-C(1): 181.0(4)
Bonds	P(1)-C(2): 180.00(18)	P(1)-C(2): 181.24(17)	P(1)-C(2): 182.2(7)	P(1)-C(2): 180.9(3)	P(1)-C(2): 181.1(6)	P(1)-C(2): 180.2(4)
	P(1)-C(3): 182.64(16)	P(1)-C(3): 181.55(16)	P(1)-C(3): 182.4(7)	P(1)-C(3): 182.9(3)	P(1)-C(3): 183.4(6)	P(1)-C(3): 182.0(3)
Ring bonds	C(3)-C(4): 138.9(2)	C(3)-C(4): 139.0(2)	C(3)-C(4): 139.8(10)	C(3)–C(4): 138.6(4)	C(3)-C(4): 137.8(8)	C(3)-C(4): 139.3(5)
	C(3)-C(8): 139.7(2)	C(3)-C(8): 140.0(2)	C(3)-C(8): 138.9(10)	C(3)-C(8): 138.6(4)	C(3)-C(8): 139.2(8)	C(3)-C(8): 138.8(5)
	C(4)-C(5): 137.8(2)	C(4)-C(5): 138.2(2)	C(4)-C(5): 137.2(11)	C(4)-C(5): 137.6(5)	C(4)-C(5): 138.1(9)	C(4)–C(5): 137.8(5)
	C(5) = C(6): 137.8(3) C(6) = C(7): 139.1(3)	C(5)=C(6): 138.7(3) C(6)=C(7): 138.3(3)	C(5)-C(6): 155.60(15) C(6)-C(7): 134.7(13)	C(5)=C(6): 137.30(6) C(6)=C(7): 138.2(6)	C(5) = C(6): 139.8(8) C(6) = C(7): 138.2(8)	C(5) = C(6): 136.8(3) C(6) = C(7): 137.2(6)
	C(7)-C(8): 137.3(3)	C(7)-C(8): 139.3(2)	C(7)-C(8): 139.5(11)	C(7)-C(8): 137.3(5)	C(7)-C(8): 137.0(8)	C(7)-C(8): 137.2(0)
Other bonds	P(1)–S(1): 195.76(7)				C(6)-C(9): 149.3(9)	
C–F bonds (av.)	C(4)-F(1): 135.6(2)	C(4)–F(1): 135.86(19)	C(5)–F(1): 137.6(10)	C(4)–F(1): 134.9(4)	C(4)–F(1): 134.0(6)	C(5)–F(1): 135.7(5)
()	C(8)–F(2): 135.1(2)		C(7)–F(2): 135.3(10)	C(8)–F(2): 136.3(4)	C(5)–F(2): 134.4(6) C(9)–F(7): 132.1(6)	
Angles at	C(1)-P(1)-C(2):	P(1) #1-Pd(1)-	P(1)-Pd(1)-P(2):	P(1)-Pd(1)-P(2):	P(1)#1-Pd(1)-P(1):	P(1)-Pd(1)-Cl(1):
Pd and P	103.70(11)	P(1):180.000(14)	94.12(7)	100.34(4)	180.0	88.19(4)
	C(1)-P(1)-C(3):	P(1) - Pd(1) - Cl(1): 87 015(15)	P(1) - Pd(1) - Cl(1): 172 25(7)	P(1)-Pd(1)-Cl(1): 172.83(3)	P(1) - Pd(1) - Cl(1):	P(1)-Pd(1)-Cl(3): 03.87(4)
	C(2)-P(1)-C(3):	P(1) #1-Pd(1)-	P(2)-Pd(1)-Cl(1):	P(2)-Pd(1)-Cl(1):	P(1)#1-Pd(1)-Cl(1):	Cl(1)-Pd(1)-Cl(3):
	107.70(9)	Cl(1):92.985(15)	86.35(7)	84.81(4)	85.49(6)	177.34(3)
		Cl(1) #1-Pd(1)-Cl(1):	P(1)-Pd(1)-Cl(2):	P(1)-Pd(1)-Cl(2):	Cl(1)#1-Pd(1)-Cl(1):	P(1)-Pd(1)-Cl(2):
		180.0	90.26(7)	85.50(4)	180.00(7)	173.32(3)
		C(1)-P(1)-C(2):	P(2)-Pd(1)-Cl(2):	P(2)-Pd(1)-Cl(2):	C(1)-P(1)-C(2):	Cl(1)-Pd(1)-Cl(2):
		$\Gamma(1) = P(1) = C(3)$	$C_{1}(1) - Pd_{1}(1) - C_{2}(2)$	$\Gamma = 1/3.42(3)$ Cl(1)=Pd(1)=Cl(2):	C(1) = P(1) = C(3)	$C_{1}(2) = Pd(1) = C_{1}(3)$
		106.11(8)	90.24(7)	89.65(4)	106.8(3)	85.79(4)
		C(2)-P(1)-C(3):	C(1)-P(1)-C(2):	C(1)-P(1)-C(2):	C(2)–P(1)–C(3):	Pd(1)-Cl(2)-Pd(2):
		104.10(8)	103.7(4)	103.70(17)	106.8(3)	92.24(4)
		C(1)-P(1)-Pd(1):	C(1)-P(1)-C(3):	C(1)-P(1)-C(3):	C(1)-P(1)-Pd(1):	Pd(1)-Cl(3)-Pd(2):
		C(2) = P(1) = Pd(1)	C(2)=P(1)=C(3)	P(1) = P(1) = C(3)	C(2)=P(1)=Pd(1)	P(1) = P(1) = C(2)
		112.69(6)	100.6(4)	108.15(15)	114.2(2)	104.19(19)
		C(3)–P(1)–Pd(1):	C(1)–P(1)–Pd(1):	C(1)–P(1)–Pd(1):	C(3)–P(1)–Pd(1):	C(1)-P(1)-C(3):
		115.85(5)	116.5(3)	112.74(12)	110.47(18)	106.68(17)
			C(2)-P(1)-Pd(1):	C(2)=P(1)=Pd(1):		C(2) = P(1) = C(3):
			C(3)=P(1)=Pd(1)	C(3)=P(1)=Pd(1)		C(1) = P(1) = Pd(1)
			113.3(2)	119.13(10)		114.06(13)
						C(2)–P(1)–Pd(1):
						115.26(13)
						C(3)-P(1)-Pd(1):
Angles	C(4) - C(3) - C(8)	C(4) - C(3) - C(8)	C(4) - C(3) - C(8)	C(4) - C(3) - C(8)	C(4) = C(3) = C(8)	108.29(11) C(4)-C(3)-C(8)
(int.) ring	113.90(15)	116.75(14)	120.6(7)	114.2(3)	114.9(5)	119.7(3)
0	C(5)-C(4)-C(3):	C(5)-C(4)-C(3):	C(5)-C(4)-C(3):	C(5)-C(4)-C(3):	C(5)-C(4)-C(3):	C(5)-C(4)-C(3):
	124.19(16)	123.67(15)	118.2(8)	123.7(3)	122.3(5)	118.1(3)
	C(6)-C(5)-C(4):	C(6)-C(5)-C(4):	C(6)-C(5)-C(4):	C(6)-C(5)-C(4):	C(6)-C(5)-C(4):	C(6)-C(5)-C(4):
	118.90(19) C(5)_C(6)_C(7)·	118.08(15) C(5)-C(6)-C(7)	122.9(9) C(7)-C(6)-C(5):	118.9(3)	121.9(5)	123.4(4) C(5)_C(6)_C(7):
	120.19(18)	120.45(16)	117.9(8)	120.7(3)	116.1(5)	117.8(3)
	C(6)-C(7)-C(8):	C(6)-C(7)-C(8):	C(6)-C(7)-C(8):	C(6)-C(7)-C(8):	C(6)-C(7)-C(8):	C(6)-C(7)-C(8):
	118.21(18)	120.25(16)	123.5(9)	117.6(3)	121.0(5)	121.2(4)
	C(3)–C(8)–C(7):	C(3)–C(8)–C(7):	C(3)–C(8)–C(7):	C(3)–C(8)–C(7):	C(3)–C(8)–C(7):	C(3)–C(8)–C(7):
	124.58(19)	120.79(16)	117.0(8)	124.9(3)	123.8(5)	119.7(4)

[a] Symmetry transformations used to generate equivalent atoms: -x + 1, -y + 1, -z + 1.

	12	18	19	21	22	23
Empirical formula	C ₁₆ H ₁₇ F ₂ NOP ₂ S ₂	$C_{16}H_{20}Cl_2F_2P_2Pd$	$C_{16}H_{18}Cl_2F_4P_2Pd$	C ₁₆ H ₁₈ Cl ₂ F ₄ P ₂ Pd·CHC	$l_{3}C_{18}H_{12}Cl_{2}F_{14}P_{2}Pd$	$C_{16}H_{20}Cl_4F_2P_2Pd_2$
Formula weight	403.37	489.56	525.54	644.91	733.52	666.86
Temperature [K]	172(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Radiation [Å]	Mo- K_{α} (0.71073)	Mo- K_{α} (0.71073)	Mo- K_{α} (0.71073)	Mo- K_{α} (0.71073)	Mo- K_a (0.71073)	Mo- K_{α} (0.71073)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group Cell dimensions	$P2_1/n$	$P2_{1}/c$	PĪ	$P2_{1}/c$	$P2_{1}/c$	$P2_1/n$
<i>a</i> [pm]	804 50(10)	715 60(10)	796 8(2)	956 45(19)	623 6(3)	1364 4(3)
h [pm]	1132.2(3)	963 60(10)	901 4(10)	2842.9(6)	748 0(3)	1127.2(2)
c [pm]	1980 9(3)	1408 40(10)	1586 3(3)	942.00(19)	2543 6(15)	1571 6(3)
a [°]	90	90	85 47(10)	90	90	90
β [°]	95.790(10)	103.870(10)	80.62(2)	111.74(3)	90.83(3)	114.37(3)
v [°]	90	90	63.86(10)	90	90	90
Volume [nm ³]	1.7951(6)	0.94285(18)	1.0091(3)	2.3791(8)	1.1862(10)	2.2016(8)
Z	4	2	2	4	2	4
d (calcd.) [mg/m ³]	1493	1.724	1.730	1.801	2.054	2.012
$\mu [{\rm mm}^{-1}]$	498	1.450	1.375	1.510	1.260	2.280
Crystal size [mm ³]	$0.70 \times 0.50 \times 0.20$	$0.60 \times 0.20 \times 0.10$	$0.90 \times 0.20 \times 0.02$	$0.40 \times 0.20 \times 0.20$	$0.80 \times 0.60 \times 0.50$	$0.40 \times 0.20 \times 0.10$
Theta range [°]	2.65 to 27.51	2.59 to 27.50	2.52 to 24.99	2.29 to 26.01	2.84 to 27.50	2.44 to 26.05
Range in $h k l$	$-1 \le h \le 10$	$-9 \le h \le 9$	$-9 \le h \le 1$	$-11 \le h \le 11$	$-1 \le h \le 8$	$-16 \le h \le 16$
C	$-14 \le k \le 14$	$-12 \le k \le 12$	$-10 \le k \le 10$	$-34 \le k \le 34$	$-1 \le k \le 9$	$-13 \le k \le 13$
	$-25 \le l \le 25$	$-18 \le l \le 18$	$-18 \le l \le 18$	$-11 \le l \le 11$	$-33 \le l \le 32$	$-19 \le l \le 19$
Refl. collected	5509	8562	4454	25010	3975	14946
Independent refl.	4082, $R_{\rm int} = 0.0394$	2176, $R_{\rm int} = 0.0292$	3551, $R_{\rm int} = 0.0335$	4360, $R_{\rm int} = 0.0496$	2705, $R_{\rm int} = 0.0403$	4280, $R_{\rm int} = 0.0342$
Refl. $I > 2 \sigma(I)$	2615					
Restr. / parameters	0 / 225					
$R_1^{[a]}[I \ge 2\sigma(I)]$	0.0573	0.0177	0.0542	0.0274	0.0515	0.0235
$wR_2^{[b]}[I > 2\sigma(I)]$	0.1033	0.0435	0.1274	0.0758	0.1311	0.0499
$R_1^{[a]}$ (all data)	0.1350	0.0198	0.0873	0.0346	0.0585	0.0375
$wR_2^{[b]}$ (all data)	0.1524	0.0444	0.1274	0.0786	0.1396	0.0556
$\operatorname{GooF}^{[c]}(F_{o}^{2})$	0.995	1.076	0.983	1.080	1.156	0.992
Largest diff. peak	0.529 [eÅ ⁻³]	0.376 [eÅ ⁻³]	0.812 [e Å ⁻³]	0.467 [eÅ ⁻³]	1.021 [eÅ ⁻³]	0.450 [e Å ⁻³]
Largest diff. hole	–0.479 [eÅ ⁻³]	-0.434 [eÅ ⁻³]	-1.462 [eÅ ⁻³]	-0.484 [eÅ ⁻³]	-1.358 [eÅ ⁻³]	-0.413 [eÅ ⁻³]

Table 6. Experimental and X-ray crystallographic data for compounds 12, 18, 19 and 21–23.

 $[a] R_1 = \Sigma ||F_{obsd.}| - |F_{calcd.}|| / \Sigma |F_{obsd.}|. [b] wR_2 = \{ \Sigma [w(F_{obsd.}^2 - F_{calcd.}^2)^2] / \Sigma [w(F_{obsd.}^2)^2] \}^{1/2}. [c] GooF = \{ \Sigma [w(F_{obsd.}^2 - F_{calcd.}^2) / (n-p) \}^{1/2}.$

5	+ trans-[(PhCN)2PdCl2]	>	1/2 [(3-FC ₆ H ₄ PMe ₂)PdCl ₂] ₂
		-2 PhCN C ₆ H ₆ , 20 °C,	23 , 83 %
		2 h	

Scheme 7.



Figure 10. X-ray structure of 23.

substrate selectivities and regioselectivities exhibited by these substrates with Me₂PSiMe₃, Me₂PSnMe₃ or Me₂PLi in C₆D₆ or cyclohexane indicate the fluorine substituent effects sequence $f_{o-F} > f_{m-F}$ which is not typical for nucleophilic replacement of fluorine in polyfluoroarenes, conventionally considered to proceed through a two-step Meisenheimer S_NAr mechanism. Quantum-chemical calculations, however, predict that the reactions under study should each occur through a concerted A_ND_N mechanism with a single TS. Dimethyl(polyfluorophenyl)phosphanes have been shown to be suitable ligands for the preparation of phosphanepalladium dichloride complexes.

Experimental Section

General: Because of the air- and moisture-sensitivities of the Me₃-MEMe₂ compounds (M = Si, Sn; E = As, P, N) and the resulting (polyfluoroaryl)phosphanes, as well as their expected toxicities, all experiments were carried out with use of high-vacuum and Schlenk techniques. The glassware used was thoroughly heated and evacuated. The NMR spectra were recorded with a Bruker AC 200 (¹H: 200.13 MHz, ¹⁹F: 188.31 MHz, ³¹P: 81.02 MHz) or Bruker AV 300 (1H: 300.13 MHz, 19F: 282.39 MHz, 31P: 121.49 MHz) spectrometer. Mass spectra of the new compounds were obtained with a Varian MAT 212 mass spectrometer. The fragmentation data are given together with the preparative procedure for the individual products. HRMS were obtained with a GC/MS-System [GCToF, Mikromass; column HPS 25 m; temperature changes: starting at 40 °C (1 min), increase 10 °C min⁻¹, finishing at 300 °C]. Far-infrared spectra were recorded in the form of polyethylene pellets with a Perkin-Elmer 1800 FT infrared spectrometer.



Structural Investigations: The crystallographic data for compounds 12, 18, 19 and 22 were collected with a SIEMENS P4 diffractometer and the data for 21 and 23 were collected with a STOE IPDS diffractometer; both were fitted with graphite monochromators. For the data for 12, 19, 21, 22 and 23 an absorption correction was applied with the aid of the program DIFABS.^[21] All structures were solved by direct methods and refined based on F^2 by use of the SHELX program package.^[22] All hydrogen atoms were placed on calculated positions and allowed to ride on their corresponding carbon atoms with isotropic thermal parameters of 1.5 times the value for U_{eq} of the bonding atom in case of the methyl protons and of 1.2 times the value for U_{eq} of the bonding atoms were refined anisotropically.

CCDC-737603 (for 12), -737605 (for 18), -737606 (for 19), -737604 (for 21), -737601 (for 22) and -737602 (for 23) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparations and Characterization of (Dimethylphosphanyl)fluorobenzene Ligands and Selected Palladium Complexes

1-(Dimethylphosphanyl)-3-fluorobenzene (5): Compound **1** (0.34 g, 3.0 mmol) and Me₃SiPMe₂ (0.101 g, 0.75 mmol) were condensed into a liquid-nitrogen-cooled evacuated glass ampoule. The reactor was sealed and kept at 190 °C for 70 h. The volatile components (Me₃SiF and **1**) were distilled off under argon while the bath temperature was increased to 130 °C, and **5** was obtained as a colour-less liquid by vacuum distillation (0.7 mbar) at bath temperatures increasing from 20 to 35 °C (yield 0.074 g, 63%). ¹H NMR (200 MHz, C₆D₆): δ = 6.4–7.2 (4 H, CH), 1.06 [dm, ²*J*(P,H) = 3.1 Hz, 6 H, CH₃] ppm. ¹⁹F NMR (188 MHz, C₆D₆): δ = –111.4 (m) ppm. ³¹P NMR (81 MHz, C₆D₆): δ = –43.3 (br. s) ppm.

1-(Dimethylphosphanyl)-2-fluorobenzene (6): Compound **2** (0.23 g, 2.0 mmol) and Me₃SiPMe₂ (0.13 g, 1.0 mmol) were condensed into a liquid-nitrogen-cooled evacuated glass ampoule. The reactor was sealed and kept at 170 °C for 72 h. The volatile components (Me₃. SiF and **2**) were distilled off under argon while the bath temperature was increased to 130 °C, and **6** was obtained as a colourless liquid by vacuum distillation (0.7 mbar) at bath temperatures increasing from 20 to 35 °C (yield 0.11 g, 70%). ¹H NMR (200 MHz, C₆D₆): $\delta = 6.7-7.5$ (4 H, CH), 1.20 [dm, ²*J*(P,H) = 3.8 Hz, 6 H, CH₃] ppm. ¹⁹F NMR (188 MHz, C₆D₆): $\delta = -102.3$ [dm, ³*J*(P,F) = 34.3 Hz] ppm. ³¹P NMR (81 MHz, C₆D₆): $\delta = -51.4$ [dm, ³*J*(P,F) = 34.3 Hz] ppm.

1-(Dimethylphosphanyl)-3,5-difluorobenzene (7): Compound **3** (0.26 g, 2.0 mmol) and Me₃SiPMe₂ (0.13 g, 1.0 mmol) were condensed into a liquid-nitrogen-cooled evacuated glass ampoule. The reactor was sealed and kept at 190 °C for 24 h. The volatile components (Me₃SiF and **3**) were distilled off under argon while the bath temperature was increased to 130 °C, and 7 was obtained as colourless liquid by vacuum distillation (0.7 mbar) at bath temperatures increasing from 20 to 35 °C (yield 0.07 g, 42%). ¹H NMR (200 MHz, C₆D₆): δ = 6.8 [tm, ³*J*(P,H) \approx ³*J*(F,H) \approx 6.1 Hz, 2 H, CH], 6.5 [tt, ³*J*(F,H) = 8.9, ⁴*J*(H,H) = 2.0 Hz, 1 H, CH], 0.94 [d, ²*J*(P,H) = 3.3 Hz, 6 H, CH₃] ppm. ¹⁹F NMR (188 MHz, C₆D₆): δ = -111.3 (m) ppm. ³¹P NMR (81 MHz, C₆D₆): δ = -40.4 (m) ppm.

1-[Bis(methylthio)phosphanyl]-3-fluorobenzene (10): A mixture of **5** (0.10 g, 0.64 mmol), S_8 (0.025 g, 0.78 mmol) and benzene (0.6 mL) was heated at 90–100 °C for 1 h. After the mixture had cooled to room temperature, C_6D_6 was distilled off in vacuo (0.7 mbar) and the residue was dissolved in CHCl₃ (0.2 mL) and filtered. The re-

sulting solution was diluted with pentane (1 mL), and the precipitated white crystals were filtered off, washed with pentane and dried in vacuo to give **10** (0.07 g, 58%); m.p. 45–46 °C. ¹H NMR (200 MHz, C₆D₆): δ = 7.19 (m, 1 H, CH), 7.47 (m, 1 H, CH), 7.54– 7.74 (2 H, CH), 1.97 [dm, ²*J*(P,H) = 13.2 Hz, 6 H, CH₃] ppm. ¹⁹F NMR (188 MHz, C₆D₆): δ = -112.1 (m) ppm. ³¹P{¹H} NMR (81 MHz, C₆D₆): δ = 33.9 [d, ⁴*J*(P,F) = 5 Hz] ppm. MS (70 eV, EI): *m/z* (%) = 188 (100) [M]⁺, 173 (85) [M – Me]⁺, 155 (12) [M – S – H]⁺. HRMS: calcd. for C₈H₁₀FPS [M] 188.0225; found 188.0238.

Dichlorobis[(3-fluorophenyl)dimethylphosphane]palladium (17): Phosphane 5 (0.074 g, 0.48 mmol) and C_6D_6 (1 mL) were condensed into an evacuated reaction vessel that was charged with bis(benzonitrile)-trans-dichloropalladium(II) (0.091 g, 0.24 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 2 h. The volatile components were distilled off in vacuo (0.7 mbar), and the residue was dissolved in CH₂Cl₂ (2 mL) and filtered. The resultant solution was diluted with EtOH (1 mL), and the precipitated pale yellow crystals were filtered off, washed with EtOH and dried in vacuo to give 17 (0.111 g, 95%); m.p. 168-169 °C (for a small amount of the crystals obtained) and 173-175 °C (for the bulk of the product). ¹H NMR (300 MHz, CDCl₃): $\delta = 6.6-7.6$ (CH; 4 H cis- and 4 H trans-17), 1.78 [d, ²J(P,H) = 11.3 Hz, 6 H, CH₃, *cis*-17], 1.74 [t, ${}^{2}J(P,H) \approx {}^{4}J(P,H) \approx 3.6$ Hz, 6 H, CH₃, *trans*-17] ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -111.2 (m, cis-17), -112.5 (m, trans-17) ppm. ³¹P{¹H} NMR (11 MHz, CDCl₃): $\delta = 6.5$ [d, ⁴*J*(P,F) = 3.7 Hz, *cis*-17, 38%], -3.9 [t, ²*J*(P,P) $\approx {}^{4}J(P,F) \approx 2.1$ Hz, trans-17, 62%] ppm. IR (polyethylene, v_{Pd-Cl}): $\tilde{v} = 351, 309, 281 \text{ cm}^{-1}$. C₁₆H₂₀Cl₂F₂P₂Pd (489.61): calcd. C 39.25, H 4.12; found C 39.13, H 4.15.

Dichlorobis[(2-fluorophenyl)dimethylphosphane]palladium (18): Phosphane 6 (0.078 g, 0.5 mmol) and C_6D_6 (1 mL) were condensed into an evacuated reaction vessel, charged with bis(benzonitrile)trans-dichloropalladium(II) (0.096 g, 0.25 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 1 h. The volatile components were distilled off in vacuo (0.7 mbar) and the residue was dissolved in CH2Cl2 (2 mL) and filtered. The resultant solution was diluted with EtOH (1 mL) and the precipitated pale yellow crystals were filtered off, washed with EtOH and dried in vacuo to give 18 (0.116 g, 95%); m.p. 189-193 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.85–8.0 (CH, 4 H *cis*- and 4 H *trans*-18), 1.87 [d, ${}^{2}J(P,H) = 11.9$ Hz, 6 H, CH₃, *cis*-18], 1.83 [t, ${}^{2}J(P,H) \approx$ ${}^{4}J(P,H) \approx 3.5 \text{ Hz}, 6 \text{ H}, \text{ CH}_{3}, \text{ trans-18} \text{ ppm}. {}^{19}\text{F} \text{ NMR} (282 \text{ MHz},$ CDCl₃): $\delta = -102.8$ (br. s, *cis*-18), -103.7 (br. s, *trans*-18) ppm. ³¹P{¹H} NMR (11 MHz, CDCl₃): $\delta = 2.1$ [d, ³J(P,F) = 13.4 Hz, *cis*-18, 58%], -4.3 [t, ${}^{2}J(P,P) \approx {}^{3}J(P,F) \approx 2.5$ Hz, *trans*-18, 42%] ppm. IR (polyethylene, v_{Pd-Cl}): $\tilde{v} = 358$, 309, 294 cm⁻¹. C₁₆H₂₀Cl₂F₂P₂Pd (489.61): calcd. C 39.25, H 4.12; found C 39.46, H 4.11.

Dichlorobis[(3,5-difluorophenyl)dimethylphosphane]palladium (19): Phosphane 7 (0.063 g, 0.36 mmol) and C₆D₆ (0.7 mL) were condensed into an evacuated reaction vessel, charged with bis(benzonitrile)-*trans*-dichloropalladium(II) (0.069 g, 0.18 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 1 h. The volatile components were distilled off in vacuo (0.7 mbar) and the residue was dissolved in CH₂Cl₂ (1 mL) and filtered. The resultant solution was diluted with EtOH (2 mL) and the precipitated pale yellow crystals were filtered off, washed with EtOH and dried in vacuo to give **19** (0.084 g, 88%); m.p. 209–213 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.15–7.33 (2 H, CH), 6.85 [tt, ³*J*(F,H) = 8.8, ³*J*(H,H) = 2.3 Hz, 1 H, CH, *trans*-**19**), 7.15–7.32, 6.70–6.82 (3 H, CH, *cis*-**19**), 1.76 [t, ²*J*(P,H) ≈ ⁴*J*(P,H) ≈ 3.4 Hz, 6 H, CH₃, *trans*-**19**], 1.82 [d, ²*J*(P,H) = 11.6 Hz, 6 H, CH₃, *cis*-**19**]

ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -106.8 (m, *cis*-**19**), -108.7 (m, *trans*-**19**) ppm. ³¹P{¹H} NMR (11 MHz, CDCl₃): δ = -1.9 (m, *trans*-**19**, 88%), 8.0 [t, ⁴*J*(P,F) = 4.7 Hz, *cis*-**19**, 12%] ppm. IR (polyethylene, v_{Pd-Cl}): \tilde{v} = 358, 309, 288 cm⁻¹. C₁₆H₁₈Cl₂F₄P₂Pd (525.59): calcd. C 36.56, H 3.45; found C 36.85, H 3.36.

Dichlorobis[(2,3-difluorophenyl)dimethylphosphane]palladium (20): Phosphane 8 (0.020 g, 0.115 mmol) and C_6D_6 (0.5 mL) were condensed into an evacuated reaction vessel, charged with bis(benzonitrile)-trans-dichloropalladium(II) (0.022 g, 0.057 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 2 h. The volatile components were distilled off in vacuo (0.7 mbar) and the residue was dissolved in CH₂Cl₂ (1 mL) and filtered. The resultant solution was diluted with EtOH (2 mL) and the precipitated pale yellow crystals were filtered off, washed with EtOH and dried in vacuo to give 20 (0.026 g, 87%); m.p. 192-200 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.0–7.7 (CH; 3H *cis*- and 3H trans-20), 1.98 [d, ${}^{2}J(P,H) = 11.8$ Hz, 6 H, CH₃, cis-20], 1.89 $[dt, {}^{2}J(P,H) \approx {}^{4}J(P,H) \approx 3.7, {}^{5}J(F,H) = 1.0 \text{ Hz}, 6 \text{ H}, \text{ CH}_{3}, \text{ trans-}$ **20**] ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -129.0$ (m), -136.4 (m, *cis*-20), -129.6 [dm, ${}^{3}J(F,F) = 21.8$ Hz], -138.1 (m, *trans*-20) ppm. ³¹P{¹H} NMR (11 MHz, CDCl₃): $\delta = -3.2$ (m, trans-20, 69%), 2.7 $[dt, {}^{3}J(P,F) = 12.3, {}^{2}J(P,P) \approx {}^{4}J(P,F) \approx 5.24 \text{ Hz}, \text{ cis-20}, 31\%] \text{ ppm.}$ IR (polyethylene, v_{Pd-Cl}): $\tilde{v} = 363$, 308 cm⁻¹. $C_{16}H_{18}Cl_2F_4P_2Pd$ (525.59): calcd. C 36.56, H 3.45; found C 36.34, H 3.28.

Dichlorobis[(2,6-difluorophenyl)dimethylphosphane]palladium (21): Phosphane 9 (0.056 g, 0.32 mmol) and C_6D_6 (0.5 mL) were condensed into an evacuated reaction vessel, charged with bis(benzonitrile)-trans-dichloropalladium(II) (0.061 g, 0.16 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 2 h. The volatile components were distilled off in vacuo (0.7 mbar) and the residue was dissolved in CH₂Cl₂ (1 mL) and filtered. The resultant solution was diluted with EtOH (2 mL) and the precipitated pale yellow crystals were filtered off, washed with EtOH and dried in vacuo to give 21 (0.060 g, 71%); m.p. 205-209 °C. ¹H NMR (30 MHz, CDCl₃): δ = 7.28–7.44 (CH; 1 H *cis*- and 1 H *trans*-21), 6.90 [tt, ${}^{3}J(F,H) = 8.5$, ${}^{3}J(H,H) \approx {}^{4}J(P,H) \approx 1.5$ Hz, 2 H, CH, trans-21], 6.75 [dt, ${}^{3}J(F,H) = 8.6$, ${}^{3}J(H,H) = 2.8$ Hz, 2 H, CH, *cis*-21], 1.90 [hept, ${}^{5}J(F,H) \approx {}^{6}J(H,H) \approx {}^{2}J(P,H) \approx {}^{4}J(P,H) \approx 1.8$ Hz, 6 H, CH₃, trans-21, 56%], 2.02 [dt, ${}^{2}J(P,H) = 11.8$, ${}^{5}J(F,H) =$ 2.1 Hz, 6 H, CH₃, *cis*-21, 44 %] ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -99.8$ (br. s, *cis- and trans-21*) ppm. ³¹P{¹H} NMR (121 MHz, CDCl₃): $\delta = -7.2$ (m, trans-21), 2.4 (m, cis-21) ppm. IR (polyethylene, v_{Pd-Cl}): $\tilde{v} = 366$, 305, 292 cm⁻¹. $C_{16}H_{18}Cl_2F_4P_2Pd$ (525.59): calcd. C 36.56, H 3.45; found C 36.54, H 3.44.

Dichlorobis{dimethyl[2,3,4,5-tetrafluoro-4-(trifluoromethyl)phenyllphosphane}palladium (22): Dimethyl[2,3,4,5-tetrafluoro-4-(trifluoromethyl)phenyl]phosphane (0.443 g, 1.56 mmol) and C₆H₆ (5 mL) were condensed into an evacuated reaction vessel, charged with bis(benzonitrile)-trans-dichloropalladium(II) (0.295 g, 0.77 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 0.5 h, filtered and concentrated in vacuo to a volume of 2 mL. The resultant solution was diluted with pentane (7 mL) and the precipitated pale yellow crystals were filtered off, washed with pentane and dried in vacuo to give 22 (0.500 g, 88%); m.p. 154–157 °C. ¹H NMR (200 MHz, CDCl₃): δ = 1.98 (m) ppm. ¹⁹F NMR (188 MHz, CDCl₃): $\delta = -57.9$ [t, ³*J*(F,F) = 17.3 Hz, 3 F, CF₃], -128.1 (m, 2 F, CF), -139.9 (m, 2 F, CF) ppm. ${}^{31}P{}^{1}H$ NMR (81 MHz, CDCl₃): δ = 2.4 (s) ppm. IR (polyethylene, v_{Pd-Cl}): \tilde{v} = 357, 307 cm⁻¹. C₁₈H₁₂Cl₂F₁₄P₂Pd (733.55): calcd. C 29.47, H 1.65; found C 29.74, H 1.57.

Di-μ-chloro{dichlorobis[(3-fluorophenyl)dimethylphosphane]}dipalladium(II) (23): Phosphane **5** (0.035 g, 0.224 mmol) and C₆D₆ (1 mL) were condensed into an evacuated reaction vessel, charged with bis(benzonitrile)-*trans*-dichloropalladium(II) (0.086 g, 0.224 mmol) and cooled with liquid nitrogen. The resulting solution was stirred at 20 °C for 2 h. The volatile components were distilled off in vacuo (0.7 mbar) and the residue was dissolved in CH₂Cl₂ (2 mL) and filtered. The resultant solution was diluted with EtOH (1 mL) and the precipitated red crystals were filtered off, washed with EtOH and dried in vacuo to give 23 (0.062 g, 83%); m.p. 217-218 °C (became dark at 157-160 °C). ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3): \delta = 7.4-7.6 (3 \text{ H}, \text{ CH}), 7.22 \text{ (m, 1 H, CH)},$ $1.82 \text{ [d, }^{2}J(P,H) = 13.2 \text{ Hz}, 6 \text{ H}, \text{ CH}_{3} \text{ ppm}.$ ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -111.1$ (m) ppm. ³¹P{¹H} NMR (121 MHz, CDCl₃): $\delta = 14.9 \text{ [d, } {}^{4}J(\text{P,F}) = 4.2 \text{ Hz] ppm. } \text{C}_{16}\text{H}_{20}\text{Cl}_{4}\text{F}_{2}\text{P}_{2}\text{Pd}_{2} \text{ (666.93):}$ calcd. C 28.82, H 3.02; found C 28.98, H 2.92.

Competitive Reactions of 1 and 2 or 3 and 4 with Me₃EPMe₂ (E = Si, Sn): Me₃EPMe₂ (E = Si or Sn, 0.3–0.5 mmol), an equimolar mixture of di- or trifluorobenzenes (0.6–1.5 mmol) and the solvent (0.5 mL) were condensed into an evacuated NMR tube cooled with liquid nitrogen. The tube was sealed under vacuum, allowed to warm to ambient temperature and then kept at the temperatures specified in Schemes 2 and 3 while NMR spectra were periodically recorded.

Reaction between 4 and Me₃SiNMe₂: Me₃SiNMe₂ (0.059 g, 0.5 mmol), 4 (0.132 g, 1.0 mmol) and C_6H_6 (0.3 mL) were condensed into an evacuated NMR tube cooled with liquid nitrogen. The tube was sealed under vacuum, allowed to warm to ambient temperature and then kept at the temperature specified in Scheme 4 while NMR spectra were periodically recorded. In the ¹⁹F NMR spectrum, the known isomer 14^[23] leads to the signal at $\delta_{\rm F} = -122.0$ (s, 2 F) ppm; the newly prepared isomer 13 gives $\delta_{\rm F} = -141.0$ (m, 1 F), -151.4 (m, 1 F) ppm. After 40 h at 190 °C the reaction mixture contained 85 and 15% of the compounds 13 and 14, respectively. The volatile components (Me₃SiF, C₆H₆ and 4) were distilled off and a mixture of 13 and 14 was obtained as a colourless liquid by vacuum distillation (0.7 mbar) at bath temperatures increasing up to 50 °C (yield 0.057 g, 72%). Two thirds of the mixture were distilled off to give 13 of 96% purity. ¹H NMR (200 MHz, CDCl₃): δ = 6.83–6.99 (1 H, CH), 6.50–6.74 (2 H, CH), 2.86 [d, ⁵J(F,H) = 0.6 Hz, 6 H, CH₃] ppm. ¹⁹F NMR (188 MHz, CDCl₃): δ = -140.3 (m, 1 F), -150.8 [dt, ${}^{3}J(F,F) = 18.8$, ${}^{4}J(F,H) = 9.3$ Hz, 1 F] ppm. HRMS: calcd. for C₈H₉NF₂ [M] 157.07030; found 157.07045.

Competitive Reactions of 3 and 4 with Me₃SiNMe₂: Me₃SiNMe₂ (0.059 g, 0.5 mmol), 3 (0.132 g, 1.0 mmol), 4 (0.132 g, 1.0 mmol) and C₆H₆ (0.5 mL) were condensed into an evacuated NMR tube cooled with liquid nitrogen. The ampoule was sealed under vacuum, allowed to warm to ambient temperature and then kept at the temperature specified in Scheme 5 while NMR spectra were periodically recorded. In the ¹⁹F NMR spectrum the known isomer 15^[24] is characterized by the signal at $\delta_{\rm F} = -112.7$ (s) ppm.

Competitive Reactions of 3 and 4 with Me₂PLi: Me₂PH (0.12 g, 2.0 mmol) was condensed into an evacuated reaction vessel, charged with 0.5 mL of a 2.7 molar solution of *n*BuLi (1.35 mmol) in heptane and cooled with liquid nitrogen. The mixture was allowed to warmed up to ambient temperature and stirred at 20 °C for 1 h. The volatile components were distilled off in vacuo, the remaining white Me₂PLi was cooled with liquid nitrogen, and an equimolar mixture of the trifluorobenzenes **3** and **4** (2.7 mmol) and C₆D₆ (0.5 mL) were condensed into the reaction vessel. The mixture was allowed to warm to ambient temperature, stirred for 0.5–2 h and analysed by ³¹P and ¹⁹F NMR spectroscopy and CMS (see Scheme 4).



Supporting Information (see also the footnote on the first page of this article): Quantum chemical results (calculated energies, structures and lowest frequencies for transition states)

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- L. I. Goryunov, J. Grobe, V. D. Shteingarts, B. Krebs, A. Lindemann, E.-U. Würthwein, C. Mück-Lichtenfeld, *Chem. Eur. J.* 2000, 6, 4612–4622.
- [2] L. I. Goryunov, V. D. Shteingarts, J. Grobe, B. Krebs, M. U. Triller, Z. Anorg. Allg. Chem. 2002, 628, 1770–1779.
- [3] a) J. Grobe, L. I. Goryunov, V. D. Shteingarts, Russ. J. Org. Chem. 2005, 41, 1744–1745; b) L. I. Goryunov, J. Grobe, V. D. Shteingarts, R. Mews, E.-U. Würthwein, Russian, J. Org. Chem. (in press).
- [4] R. Bolton, J. P. B. Sandall, J. Fluorine Chem. 1982, 21, 459– 467.
- [5] a) Fluorine in Organic Chemistry (Ed.: R. D. Chambers), J. Wiley & Sons, New York, 1973, chapter 9; b) L. S. Kobrina, in: Fluorine Chemistry Reviews (Eds.: P. Tarrant, M. Dekker), New York, 1974, vol. 7, pp. 1–114; c) G. M. Brooke, J. Fluorine Chem. 1997, 86, 1–76.
- [6] J. Burdon, Tetrahedron 1965, 21, 3373; R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead, J. C. Tatlow, J. Chem. Soc., Chem. Commun. 1974, 239–240; R. D. Chambers, D. Close, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Chem. Soc. Perkin Trans. 1 1977, 1774–1778; R. D. Chambers, D. Close, D. L. H. Williams, J. Chem. Soc. Perkin Trans. 2 1980, 778–780; R. D. Chambers, M. J. Seabury, D. L. H. Williams, N. Hughes, J. Chem. Soc. Perkin Trans. 1 1988, 251–254; R. D. Chambers, M. J. Seabury, D. L. H. Williams, N. Hughes, J. Chem. Soc. Perkin Trans. 1 1988, 255–257.
- [7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara,

M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.01*, Gaussian, Inc., Wallingford CT, **2004**.

- [8] S. Grimme, J. Chem. Phys. 2003, 118, 9095.
- [9] The natures of these van der Waals complexes were further investigated by optimizations with Grimme's recently developed B97-D DFT functional (S. Grimme, J. Comp. Chem. 2006, 27, 1787) with application of the basis set def2-TZVP as implemented in TURBOMOLE 6.0 (TURBOMOLE: R. Ahlrichs, M. Bär, H.-P. Baron, R, Bauernschmitt, S. Böcker, M. Ehring, K. Eichkorn, S. Elliot, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Ohm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss, University of Karlsruhe, 2005; see also: http://www.turbomole.com) The results obtained are in good agreement with the SCS-MP2 values reported in the text, underlining the excellent suitability of both the SCS-MP2 the and DFT-D approach for investigations of weakly bound complexes.
- [10] a) A. Hunter, M. Renfrew, J. A. Taylor, J. M. J. Whitmore, A. Williams, J. Chem. Soc. Perkin Trans. 2 1993, 1703–1704; b) A. Hunter, M. Renfrew, D. Rettura, J. A. Taylor, J. M. J. Whitmore, A. Williams, J. Am. Chem. Soc. 1995, 117, 5484–5491; c) J. Shakes, C. Raymond, D. Rettura, A. Williams, J. Chem. Soc. Perkin Trans. 2 1996, 1553–1557; d) N. R. Cullum, D. Rettura, J. M. J. Whitmore, A. Williams, J. Chem. Soc. Perkin Trans. 2 1996, 1559–1563.
- [11] V. M. Vlasov, V. V. Aksenov, P. P. Rodionov, I. V. Beregovaya, L. N. Shchegoleva, *Russ. J. Org. Chem.* 2002, 38, 115–125.
- [12] M. Renfrew, J. A. Taylor, J. M. J. Whitmore, A. Williams, J. Chem. Soc. Perkin Trans. 2 1994, 2383–2384.
- [13] N. R. Cullum, A. Hunter, M. Renfrew, D. Rettura, J. A. Taylor, J. M. J. Whitmore, A. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 9200–9205.
- [14] A. Williams, Chem. Soc. Rev. 1994, 23, 93-100.
- [15] B. Chiavarino, M. E. Crestoni, S. Fornarini, F. Lanucara, J. Lemaire, P. Maitre, *Angew. Chem. Int. Ed.* 2007, 46, 1995–1998 (and references cited therein).
- [16] F. Terrier, G. Ah-Kow, M.-J. Pouet, M.-P. Simonnin, *Tetrahe*dron Lett. 1976, 227–228.
- [17] D. R. Stull, E. F. Westrum Jr., G. C. Sinke, *The Chemical Ther-modynamics of Organic Compounds*, John Wiley & Sons, New York, **1969**.
- [18] International Tables for Crystallography, vol. C (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, Boston, London, 1995.
- [19] W. P. Jencks, Acc. Chem. Res. 1980, 13, 161–169.
- [20] a) J. A. Rahn, M. S. Holt, M. O'Neil-Johnson, J. H. Nelson, *Inorg. Chem.* **1988**, 27, 1316–1320; b) E. A. Allen, W. Wilkinson, *Spectrochim. Acta Ser. A* **1974**, 30, 1219–1224.
- [21] SAINT Plus, version 6.02, Bruker AXS Inc., Madison, WI 1999.
- [22] G. M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1997.
- [23] R. J. Abraham, J. F. Busby, M. A. Cooper, Org. Magn. Reson. 1974, 6, 612–613.
- [24] A. S. Cantrell, P. Engelhardt, M. Hoegberg, S. R. Jaskunas, N. G. Johansson, C. L. Jordan, J. Kangasmetsä, M. D. Kinnick, P. Lind, J. M. Morin Jr., M. A. Muesing, R. Noreén, B. Öberg, P. Pranc, C. Sahlberg, R. J. Ternansky, R. T. Vasileff, L. Vrang, S. J. West, H. Zhang, J. Med. Chem. 1996, 39, 4261– 4274.

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