Water Soluble Phosphanes, IX[◇]

Nucleophilic Phosphanylation of Fluoroaromatic Compounds with Carboxyl, Carboxymethyl, and Aminomethyl Functionalities – an Efficient Synthetic Route to Amphiphilic Arylphosphanes

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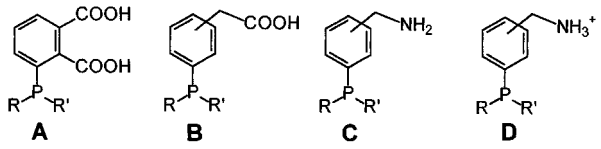
Received May 6, 1997

Keywords: Nucleophilic phosphanylation / Phosphanylphthalic acid / Phosphanylphenylacetic acid / Benzylaminophosphanes / Water solubility

Chiral- and multiply-carboxylated phosphanes and phosphanyl derivatives of benzoic and phthalic acids (**1**–**9**) are accessible in high yields by nucleophilic phosphanylation of potassium or lithium salts of commercially available fluorobenzoic and 3-fluorophthalic acids with Ph_2PH, Ph_2PK, $PhPLi_2$, $Ph(K)P-(CH_2)_3-P(K)Ph$ in superbasic media (DMSO/KOH) or in THF and DME. The hitherto unknown phosphanylphenylacetic acids (**10**–**13**) and phosphanylbenzylamines $RR'P-C_6H_4-CH_2-NH_2$ (**14**–**19**, R, R′ = H, Me, Ph) with unsubstituted amino groups were also synthesized by this method. The diphenylphosphanyl derivatives **14**–**16** (R, R′ = Ph) are accessible by an alternative method involving $LiAlH_4$ reduction of the phosphanylbenzonitriles (**20**–**22**), which were obtained in high yields by nucleophilic phosphanylation of the corresponding fluoro- or chlorobenzonitriles. The novel bidentate phosphanylbenzonitrile **23** has also been obtained using this synthetic route. All compounds were completely characterized by elemental analysis, NMR spectroscopy, and mass spectrometry.

Aromatic phosphanes with carboxylated side chains, e.g. $Ph_2P-(CH_2)_n-COOH$, $Ph_2P-C_6H_4-2$-COOH, have been extensively employed as components in catalysts for the oligomerization, polymerization, telomerization and hydroformylation of olefins[2a][2b][2c][2d]. Thus, the catalyst used for the two phase oligomerization of olefins in the "Shell higher olefin process" (SHOP)[2e] is prepared by reaction of bis(cyclooctadiene)nickel(0) with diphenylphosphanylacetic acid. Reduction/substitution reactions performed on pertechnate leads to neutral technetium(III) complexes with carboxylated phosphanes in which the phosphane ligands act as O,P-bidentate systems. The biodistribution of the corresponding ^{99m}Tc labelled species has been studied[2f].

The *o*-, *m*-, and *p*-isomers of diphenylphosphanylbenzoic acid have been reported earlier. These compounds are accessible by multistep[3a][3b][3c] or protective group synthesis[3d], but only in moderate overall yields. Despite the keen interest in these ligands, there are no reports in the literature so far on their higher carboxylated analogs (**A**) or derivatives containing CH_2 spacers between the aromatic ring and the COOH-groups ("phosphanylphenylacetic acids" **B**). Compounds of type **A**, which contain an additional set of hard donor atoms, should show enhanced solubility in water, and both of these factors are important for the application of these ligands in two-phase catalysis[4]. Ligands of type **B** contain activated CH_2 groups and, in addition, the carboxylate substituents are connected in a more flexible manner to the rigid aromatic ring systems. For the sake of comparison we have included phosphanylbenzylamines **C** in our study, and these systems contain aminomethyl groups. These groups can be protonated to give novel cationic water soluble phosphanes **D**. Ligands of this type, bearing quaternary ammonium groups, form palladium complexes with phase transfer properties. They are effective catalysts for the fluorocarbonylation of bromobenzene with CO and KF[4b].



Ligands with functionalized peripheries are of increasing interest[5a] because of their potential for further derivatization, e.g. by esterification with diols to give functionalized linear polymers suitable as insoluble supports for the immobilization of catalysts[5b].

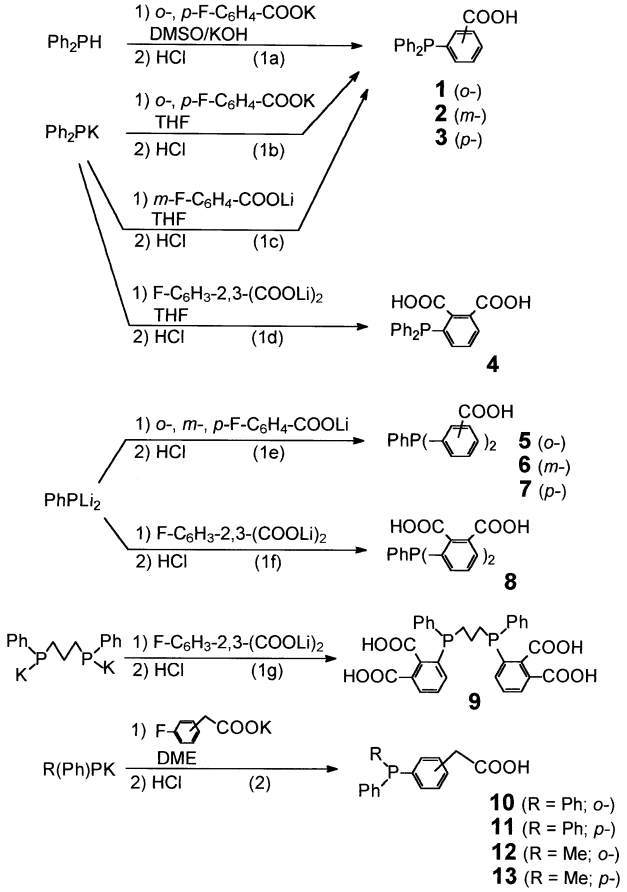
As part of a project aimed at the development of tailor made water soluble phosphanes[6] for two-phase catalysis we have developed new synthetic procedures for these ligands based on nucleophilic phosphanylation of suitable functionalized fluoro-aromatic compounds under different conditions.

[◇] Part VIII: Ref.[1].

  1434–1948/98/0101–0073 $ 17.50+.50/0

Nucleophilic Phosphanylation of Fluorobenzoic and Fluorophthalic Acids

Nucleophilic displacement of the halogen (X) in aromatic compounds X−C_6H_4−Z (X = F, Cl, Br; Z = NO_2, SO_3H, COOH) that contain electron withdrawing substituents (Z), proceeds much faster with the fluoro- than with the chloro- or bromo-compounds. This is well established for the halonitrobenzenes[7a][7b] and a variety of substituted aromatic amines has been obtained by making use of the pronounced reactivity of activated fluorobenzene derivatives towards nitrogen nucleophiles[7c]. The phosphanylation of the commercially available fluorobenzoic or fluorophthalic acids should in an analogous way lead to phosphanylbenzoic or phosphanylphthalic acids. This transformation can be performed in "superbasic" media[8], using secondary or primary phosphanes and solid KOH as the base in aprotic dipolar solvents (e.g. dimethyl sulfoxide). Alternatively, alkali metal phosphides such as Ph_2PK or $PhPLi_2$ can be employed for these nucleophilic aromatic substitution reactions in solvents like 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF).



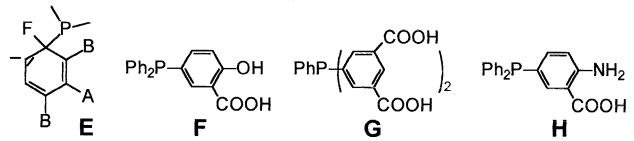
The nucleophilic phosphanylation of *p*-fluorobenzoic acid with Ph_2PH in the superbasic medium at 60 °C afforded the potassium salt of the phosphane **3** in a straightforward manner (eq. 1a). However, the corresponding reaction with the *o*-isomer gave only poor yields of **1**. Diphenylphosphane oxide $Ph_2P(H)O$[9a] and Ph_2PMe[9b] are formed by oxidation of Ph_2PH (Ph_2PK) with DMSO followed by subsequent dealkylation of the intermediate Me_2S with Ph_2PK[10] (eq. 3a,b). The potassium salt of *m*-fluorobenzoic acid did not react with Ph_2PH under these conditions. The COOK substituent in the *m*-position clearly does not activate the fluorine sufficiently for nucleophilic displacement to occur under these conditions.

$$Ph_2PH + Me_2SO \longrightarrow Ph_2P(O)H + Me_2S \quad (3a)$$

$$Me_2S + Ph_2PK \longrightarrow Ph_2PMe + MeSK \quad (3b)$$

If a solution of Ph_2PK in THF is used, then 2-F−C_6H_4−COOK could be phosphanylated to give the phosphane **1** in fair yield (eq. 1b). The *m*-isomer 3-F−C_6H_4−COOK, however, did not react at all even after prolonged reaction times. This might, at least in part, be due to the fact that 3-F−C_6H_4−COOK could not be obtained in a completely anhydrous form. 3-F−C_6H_4−COOK and 2-F−C_6H_4−COOK were prepared by neutralization of the corresponding acids with KOH in aqueous solution and heating the hydrates left after evaporation of water in vacuo at 100−120 °C for a couple of hours. The use of the anhydrous lithium salt 3-F−C_6H_4−COOLi instead of 3-F−C_6H_4−COOK resulted in phosphanylation with Ph_2PK in THF to afford **2** after work up of the reaction mixture (eq. 1c). Anhydrous 3-F−C_6H_4−COOLi can be obtained by deprotonation of the free acid with *n*BuLi or, preferably, $LiN(SiMe_3)_2$[11].

The bis(carboxyphenyl)phosphanes **5**−**7** are accessible, in an analogous way to that described above, by phosphanylation of the lithium salts of the corresponding fluorobenzoic acids with $PhPLi_2$ in THF (eq. 1e). In the case of the *m*-isomer of F-C_6H_4−COOLi, the nucleophilic aromatic substitution proceeds much slower than the corresponding reaction with the *p*- and *o*-isomers. This can be understood in terms of the different stabilization of the Meisenheimer type intermediate **E**[7b] by the COOH/COO^--substituents in the *m*- or *p*- and *o*-position to the fluoro substituent. The synthetic procedure developed for **5**−**7** can be extended to phthalic acid derivatives. Thus, nucleophilic phosphanylation of the Li-salt of 3-fluorophthalic acid with Ph_2PK or $PhPLi_2$ gave **4** or **8** after an acid workup procedure (eq. 1d,f). In the same way, Ph(K)P−$(CH_2)_3$−P(K)Ph was treated with 3-F−C_6H_3−1,2-$(COOLi)_2$ to yield the chiral bidentate tetracarboxylated phosphane **9** (eq. 1g).



The potassium salts of the phthalic acid derivatives obtained by neutralization of **4**, **8**, and **9** with KOH are highly soluble in water [0.8, 1.3, and 1.0 kg/kg water (20 °C), respectively].

Very recently we have found that carboxylated phosphanes (**1**−**7**) including salicylic, isophthalic, and anthranilic acid derivatives (**F**−**H**) can alternatively be synthesized by Pd-catalyzed P−C coupling reactions between primary

or secondary phosphanes and the corresponding functionalized iodo- or bromo-aromatic compounds[1,12].

The electron impact mass spectra of the phosphane ligands with monocarboxylated phenyl groups (**1**−**3**, **5**−**7**) all show the M^+ peak. Proximity effects[13] in the molecular ions of the *o*-carboxylated phosphanes (**1**, **5**) lead to the loss of CHO from the molecular ion. In the case of the phthalic acid derivatives **4**, **8**, and **9**, the peaks of highest *m*/*z* correspond to ions formed by loss of one or two molecules of H_2O.

Synthesis of Phosphanylphenylacetic Acids

The multiple functionality of the CH_2−COOR(H) group means that phosphanylphenylacetic acids and their esters should show an extended reactivity pattern (e.g. ester condensation) in comparison with benzoic and phthalic acid phosphanes of type **1**−**8**. This can be used for the design of tailor-made ligands with chiral backbones by the modular approach, as reported by Trost, van Vrancken and Bingel[14].

Nucleophilic phosphanylation of fluorophenylacetic acids in dimethoxyethane (DME) was employed for the synthesis of phosphanylphenylacetic acids. The intermediate of type **E**, formed in the rate determining step of these S_N2(Ar) processes, cannot be stabilized by the mesomeric effects of the substituents, and so the nucleophilic replacement is expected to proceed much slower than the analogous reaction of the fluorobenzene derivatives F−C_6H_4−Z [Z = CN (see below), COO^-, SO_3^-] with activating substituents. The weakly electron-withdrawing CH_2COO^- group can only activate the C−F bond in the *ortho* position due to its inductive effect. Thus, the reaction of the potassium salts of *o*- or *p*-fluorophenylacetic acid with Ph_2PK in DME requires 24 h reflux to give the respective isomers of diphenylphosphanylphenylacetic acid (**10**, **11**), after acidification of the reaction mixtures, in satisfactory yields (eq. 2). The P-chiral derivatives (**12**, **13**) can be prepared in an analogous way using Ph(Me)PK instead of Ph_2PK. Potassium fluorophenylacetate (*o*- or *p*-isomer) was obtained by neutralization of the appropriate free acids with a solution of KOH in methanol, followed by heating the solid left after evaporation of the solvent in vacuo (60 °C, 0.01 mbar)[15].

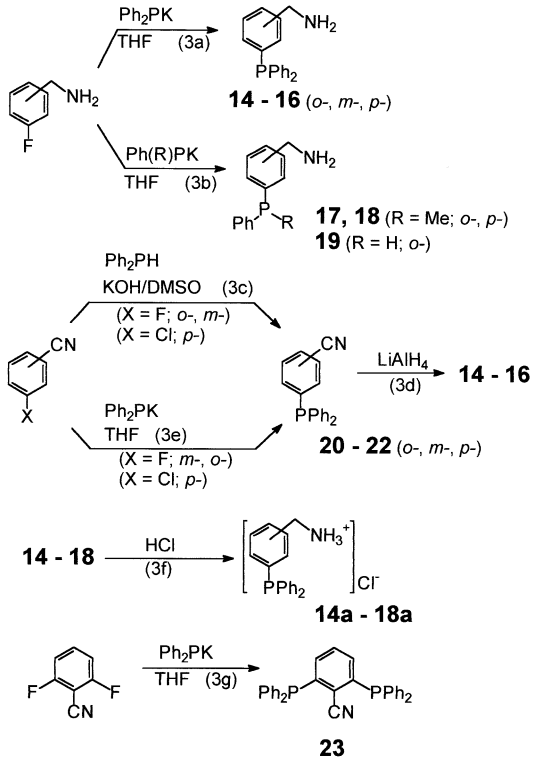
The molecular ion peaks in the mass spectra of the phosphanylphenylacetic acids are of high intensity (**10**) or represent the base peaks (**11**−**13**). The fragmentation pathway leads to the 9-phosphafluorenylium ions[16][17] at *m*/*z* = 183 or 197.

The solubilities of the alkali metal salts of the *p*-diphenylphosphanylphenylacetic acids in water (20 °C) are significantly higher than those of the corresponding *o*-isomers (e.g. Na^+ **10**: 130; Na^+ **11**: 750 g/kg water).

Synthesis of Phosphanylbenzylamines

Phosphanylbenzylamines with a primary amino group are of interest as starting materials for the synthesis of polymerizable phosphanes by acylation with acryl- or methacryloyl chloride[5a]. A new method for preparing water-soluble phosphanes by coupling of the phosphanylbenzylamine $Ph_2P-C_6H_4-CH_2$−4-NH(Me) to polyacrylic acid has very recently been reported[18]. Attempts to prepare phosphanylbenzylamines with a primary amino group by protective group synthesis via their 2,5-dimethylpyrrole derivatives or stabase (cyclic disilazane) adducts have so far been unsuccessful[5a].

We found, however, that phosphanylbenzylamines are accessible in a straightforward manner using a procedure analogous to that employed for the synthesis of the phosphanylphenylacetic acids **10**−**13**. Thus, reaction of *o*-, *m*-, or *p*-fluorobenzylamine with Ph_2PK in DME produced the phosphanes **14**−**16** in good yields. Chiral tertiary (**17** and **18**) and even secondary phosphanylbenzylamines (**19**) are accessible by this synthetic route if Ph(Me)PK or PhPHK are used instead of Ph_2PK (eq. 3a,b)[15].



The phosphanylbenzylamines **14** and **15** have been synthesized using an alternative route involving reduction of the cyanophenylphosphanes **20** and **21**[3b][3c][19] with $LiAlH_4$. The cyanophenylphosphanes are attractive starting materials since they can be obtained by a convenient method and in high yields by direct phosphanylation of the corresponding fluoro- or chlorobenzonitriles with Ph_2PH in the superbasic medium DMSO/KOH (eq. 3c,d). The same applies for the *m*-isomer **21**. Somewhat lower yields of the cyanophenylphosphanes (**20**−**22**) are obtained if the phosphanylation of the halobenzonitriles are performed with Ph_2PK in THF (eq. 3e). In both cases the nucleophilic aromatic substitution proceeds almost instantaneously, even at room temperature or below. The synthesis of the cyanophenylphosphanes **20**−**22** according to eq. 3c is therefore

superior to the methods reported in the literature[3b][3c][19].

o-Cyanophenyldiphenylphosphane (**20**) was obtained by nucleophilic phosphanylation of 2-F−C_6H_4−CN according to eq. 3c and 3e in a straightforward manner. However, attempts to synthesize this ligand by reaction of 2-Cl−C_6H_4−CN with Ph_2PM (M = Li, K) gave only very poor yields[19]. This clearly demonstrates the greater reactivity of aromatic C−F bonds towards nucleophiles in comparison with C−Cl bonds[7].The *p*-isomer (**22**) could, however, be obtained from 4-chlorobenzonitrile, indicating that the steric influence of the *o*-substituents may be decisive and override the important electronic effects. In the case of the reactive 2,5-difluorobenzonitrile, both fluoro-substituents in the *o*-positions can be replaced by the bulky Ph_2P-substituents on reaction with Ph_2PK, with the interesting bidentate ligand **23** being formed in high yield (eq. 3g).

Protonation of **14**−**18** at the amino group gives cationic phosphanes (**14a**−**18a**) (eq. 3f), and the water solublities of these compounds range from 5 to 970 g per kg of water at 20 °C. The *p*-isomers have much higher solubilities than the corresponding *ortho*-compounds. At higher temperatures thermal dissociation occurs to give the primary amines and HCl. The mass spectra obtained from **14a**−**18a** therefore show the M^+ peaks of the corresponding phosphanylbenzylamines along with that of HCl.

NMR Spectra of the Phosphane Ligands 1−23

The structural assignments given for **1**−**23** are based mainly on $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectroscopy. ^1H-NMR spectra will only be discussed in certain cases.

Table 1. $^{31}P\{^1H\}$-NMR-spectroscopical data of **1**−**23**; chemical shifts δP relative to 85% H_3PO_4; coupling constants ^1J(PH) in Hz in parentheses[a]

1	−9.6	**10**	−15.0	**17**	−35.3
2	−7.9	**11**	−4.3	**17a**	−35.7
3	−6.9	**12**	−38.0	**18**	−23.0
4	−5.2	**13**	−22.8	**19**	−48.4
5	−1.5	**14**	−14.2		(223.0)
6	−1.4	**15**	−1.7	**20**	−12.8[c], −6.7[d]
7	−1.5	**15a**	−1.7	**21**	−5.6[c], −3.6[d]
8	−5.4	**16**	−4.3	**22**	−5.7[c], −2.5[e]
9[b]	−20.5, −21.2	**16a**	−2.3	**23**	−9.8

[a] Solvents: DMSO (**1**, **3**, **5**−**7**, **20**−**22**), THF (**2**, **4**, **8**), D_2O/KOD (**9**), $CDCl_3$ (**10**, **15a**, **23**), CD_2Cl_2 (**11**−**14**, **16**, **19**, **20**, **21**), [D_6]acetone (**13**, **18**), CD_3OD (**15**, **17**, **16a**, **17a**). − [b] Diastereoisomers. − [c] Solvent DMSO. − [d] Solvent CD_2Cl_2. − [e] Solvent $CDCl_3$.

The ^{31}P-NMR shifts of the triarylphosphane-type ligands (**1**−**8**, **10**, **11**, **14**−**16**, **20**−**22**) are within a narrow range (δP = −1.4 to −15.0), and the δP values of **9**, **12**, **13**, **17**, **18** are typical for alkyl-diaryl phosphanes[20] (Table 1). In both cases the degree of substitution and the nature of the substituents has little influence on the δP values. The resonances of the *o*-isomers are shifted, in most cases, to higher field compared with those of the corresponding *m*- and *p*-isomers (c.f. **10/11**, **14/15/16**, and **20/21/22**). The bidentate carboxylated ligand **9**, containing two asymmetrically substituted phosphorus atoms, is formed as a mixture of two diastereoisomers (meso form and racemate) as indicated by two very close $^{31}P\{^1H\}$-NMR signals. The changes in the $^{31}P\{^1H\}$-NMR shift values of **14**−**17** on protonation with HCl are very small, indicating that the addition of the proton occurs preferentially at the nitrogen atom. The same also applies in the case of the $^{13}C\{^1H\}$-NMR data (c.f. **17/17a**), with the exception of δC(2)(*C*−CH_2−NH_2) (**17**: 147.0, **17a**: 138.6) (Table 2).

The assignment of the $^{13}C\{^1H\}$-NMR signals of **1**−**23** (Table 2; for the numbering scheme of the carbon atoms see Figure 1a) was achieved by comparison of the ^{13}C-shift values with those found in a series of related compounds including Ph_3P[21], Ph_2PH and $PhPH_2$[22]. The assignments were further substantiated by analysis of the proton-coupled spectra, including DEPT spectra[23], and comparison of the relative intensities of the signals. Further support for a correct assignment comes from the relative magnitude of the coupling constants ^nJ(PC), which generally decrease within the series $^2J(PC) > {}^1J(PC)$ and $^2J(PC) > {}^3J(PC) > {}^4J(PC)$[23]. The ^{13}C-NMR spectra could be analyzed using a first order approximation with $^2J(CH) < {}^3J(CH)$ and ^4J(CH) ca. 0 Hz[23]. This is shown for **8** as a representative example in Figure 1c.

The introduction of one COOH, CH_2−COOH, or CH_2−NH_2 substituent into the *o*-, *m*-, or *p*-position of the aromatic ring system causes a shift to lower field of the $^{13}C\{^1H\}$-NMR signals of the corresponding carbon atoms in comparison with those of the unsubstituted carbon atoms in the corresponding isomers and the phenyl rings, the δC values of which may be taken as an internal reference for each compound. On going from the carbonic acids to the respective potassium or sodium salts the $^{13}C\{^1H\}$-NMR spectra do not change very much, as shown for **5** and Na-**5**. The δC values of the resonances assigned to C1 and C3−C6 remain constant within 1 ppm, whereas the signal of C2 is shifted significantly (by about 2 ppm). This is in agreement with the results obtained for benzoic acid and benzoates[23a].

The $^{13}C\{^1H\}$-NMR resonances of the carbon atoms bearing a CN-substituent in **20**−**22** are shifted to higher field by between 10 and 20 ppm in comparison with those of the corresponding unsubstituted carbon atoms in the Ph-groups. This shielding effect of the CN group is well established for mono-, di-, and trisubstituted benzonitrile derivatives[23a][24].

In comparison with the corresponding δC values in phthalic acid (*C*−COOH: δ = 131.4)[25], the $^{13}C\{^1H\}$-NMR resonances of C2 [in **4**: 148.8 (32.0), **8**: 146.5 (34.4) and **9**: 147.3 (34), 147.2 (34)] are shifted drastically to lower field on the introduction of the Ph_2P or PhP(Ar) groups, while those of C4 (δ = 128.8, 129.9 or 130.0 vs. 128.6) are not changed very much. The coupling constants ^2J[PC(2)] in the substituted aromatic ring systems of **4**, **8**, and **9** are significantly greater than those in **1**, **2**, **5**, and **6**. This may be due to the pronounced steric effect of the two COOH groups in *o*- and *m*-positions which favors a conformation of the P−$C_6H_3(COOH)_2$ unit with the phosphorus lone pair in close proximity to C2 (Figure 1b). In general ^2J[PC(2)] in related systems is large when the lone pair is close to the C atom and small when it is remote[23b][23c].

Table 2. $^{13}C\{^1H\}$-NMR data of **1**−**23**[a,b,c]

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11[d]
1	134.1 (19.2)	139.3 (26.3)	130.1 (3.0)	128.5	132.0	133.6	137.4 (12.1)	133.3 (20.2)	128.5 (7.1)	128.7	167.7
2	137.6 (13.2)	133.5 (19.2)	131.1 (6.1)	129.7	128.9 (7.1)	137.2 (20.2)	136.0 (11.0)	133.2 (20.2)	128.8 (17.0)	129.1	166.8
3	142.9 (14.2)	132.9 (18.7)	129.3 (6.1)	131.0			135.8 (10.1)	133.5 (20.2)	128.9 (7.1)	129.3	167.0
4	133.5 (13)	148.8 (32)	138.4 (10)	128.8	131.5 (4)	137.5 (7)	139.3 (9)	135.2 (19)	130.2 (6)	130.5	177.3[e], 178.7[f] (2)
5	136.0 (20.4)	143.0 (26.5)	131.7 (3.1)	129.2	132.8	135.5	140.4 (12.2)	135.1 (21.4)	129.4 (8.1)	129.5	169.7
6	137.2 (13.1)	133.9 (20.2)	131.5 (6.1)	130.1	129.3 (7.1)	138.0 (19.2)	135.6 (11.1)	133.5 (20.2)	129.1 (7.1)	129.5	166.9
7	142.1 (14.2)	133.3 (19.2)	129.5 (7.1)	131.4			135.1 (10.1)	133.9 (20.2)	129.1 (8.1)	129.7	167.1
8	133.0 (14.3)	146.5 (34.4)	136.3 (7.1)	129.9	128.0 (5.0)	136.2 (7.4)	138.7 (8.1)	134.5 (19.7)	129.4 (6.7)	129.6	177.5[e], 176.0[f] (3.7)
9[h]	133.0[g] (14)[g] 132.8 (14)[g]	147.3 (34) 147.2 (34)	133.5 (8)	130.0	127.3	135.1 (8) 135.2 (8)	139.3 (8) 139.2 (8)	132.4 (17) 132.3 (17)	128.9 (6)	128.6	170.6[e] (4) 167.9[f]
10[i]	137.1 (13.2)	138.5 (27.1)	130.9 (4.4)	129.3	127.8	134.0	136.2 (9.5)	133.9 (19.8)	128.7 (7.3)	129.0	177.8
11[j]	136.2 (4)	134.4 (19.8)	130.6 (7.3)	136.7	–	–	138.2 (11.0)	134.3 (19.8)	129.4 (6.6)	129.5	172.5
12[k]	139.9 (10.3)	138.2 (27.8)	130.4 (5.1)	129.0	127.9	132.0	139.2 (13.9)	131.8 (18.3)	128.3 (5.9)	128.1	177.9
13[l]	138.9 (13.2)	132.5 (18.3)	130.0 (6.6)	132.1	–	–	140.7 (13.2)	132.3 (18.3)	128.9 (6.6)	128.7	175.0
14[m]	136.9 (9.6)	147.7 (24.0)	129.8	127.6	128.5 (5.3)	134.0	135.6 (13.4)	134.3 (19.5)	129.0 (7.1)	129.2	–
15[n]	137.9 (11.2)	133.0 (22.9)	143.9 (7.4)	128.1	129.2 (5.7)	132.5 (16.3)	137.7 (11.2)	134.2 (19.4)	129.0 (6.7)	129.2	
16[o]	136.0 (10.6)	134.5 (19.8)	127.9 (7.1)	143.9	–	–	137.8 (11.1)	134.1 (19.4)	129.0 (7.0)	129.1	
17[p]	140.7 (11.7)	147.0 (22.7)	127.5[s]	129.4[s]	128.2 (5.9)	131.1	137.3 (14.7)	132.1 (18.3)	128.7 (6.6)	128.6	
17a	140.6 (8.8)	138.6 (24.9)	130.4	130.6	131.1 (5.9)	133.3	140.4 (14.7)	133.2 (18.3)	130.2 (6.6)	130.1	
18[q]	141.1 (13.2)	132.7 (18.9)	127.6 (6.9)	144.3	–	–	138.5 (12.2)	132.2 (18.3)	128.8 (6.2)	128.6	
19[r]	135.6 (6.2)	149.5 (15.6)	128.0 (4.0)	129.8	127.0 (2.8)	133.3 (12.6)	134.6 (11.0)	134.4 (17.3)	128.7 (9.2)	128.8	
20	142.7 (19.8)	117.8 (33.0)	132.1 (10.3)	128.5	133.8 (5.1)	133.0 (20.5)	134.5 (10.3)	134.0 (20.5)	128.8 (6.6)	129.4	117.6[s] (3.7)
21	136.6 (17.6)	137.7 (20.5)	112.9 (5.9)	132.1	129.3	140.4 (16.9)	135.9 (11.0)	133.9 (20.2)	129.2 (7.3)	129.5	118.7[s]
22	145.0 (17.6)	133.4 (19.5)	131.7 (6.6)	111.9	–	–	135.6 (11.0)	134.0 (20.5)	128.8 (7.3)	129.4	118.6[s]
23[u]	144.4 (17.9)[t]	122.8 (32.8)	144.4 (17.9)[t]	133.0	131.6	133.0	134.7 (10.5)[t,v]	133.9 (20.6)[t,v]	128.7 (7.2)[t,v]	129.3	115.8[s] (3.5)

[a] Chemical shift δ(C) relative to TMS; coupling constants ^nJ(PC) in Hz in parentheses. – [b] Solvents: CD_2Cl_2 (**10**, **20**, **21**, **23**), D_2O (**8**), $CDCl_3$ (**12**, **14** − **16**, **18**, **22**), [D_6]acetone (**11**, **13**), CD_3OD (**17**, **17**·HCl), C_6H_6 (**19**); [D_6]DMSO (**1**−**4**, **6**, **7**, **9**). – [c] For an indication of the carbon atoms see Figure 1a. – [d] COOH substituent. – [e] Potassium salt; COO^- in the *o*-position. – [f] COO^- in the *m*-position to phosphorus. – [g] Diastereoisomers. – [h] $-CH_2-CH_2-CH_2$: 22.8, 22.2; $CH_2-CH_2-CH_2$: 29.5, 29.4 (13); diasteroisomers. – [i] CH_2-COOH: 39.7 (23.5). – [j] CH_2-COOH: 40.9. – [k] CH_2-COOH: 39.6 (24.1); P−*Me*: 12.4 (13.9). – [l] CH_2-COOH: 41.1; P−*Me*: 12.4 (13.9).– [m] CH_2-NH_2: 45.5 (22.1). – [n] CH_2-NH_2: 46.7. – [o] CH_2-NH_2: 46.3. – [p] CH_2-NH_2: 44.7 (22.7); P−*Me*: 12.2 (13.9). – [q] CH_2-NH_2: 46.3; P−*Me*: 13.0 (14.5). – [r] CH_2-NH_2: 48.2 (15.5). – [s] CN groups.– [t] N = ^nJ(PC) + ^mJ(PC) ; n = 1−3; m = 3−6.– [u] ^4J(PP) = 4.78 ± 0.22 Hz. – [v] C7: ^1J(PC) = 10.26, ^5J(PC) = 0.36 Hz; C8: ^2J(PC) = 20.30, ^{6}(PC) = 0.11 Hz; C9: ^3J(PC) = 7.30 Hz.

Seperate resonances are observed for the two COOH groups in the 2,3-positions in the phthalic acid derivatives. In the case of **4** and **8** the signal at δ ≈ 177.5 shows doublet fine structure [^3J(PC)] and can therefore be assigned to the COOH groups in the *o*-position with respect to the P atom. The bidentate ligand **9** is obtained as a mixture of two diastereoisomers (meso form and racemate, see above) and for this reason a doubling of the $^{13}C\{^1H\}$-NMR resonances of some of the aromatic carbon atoms (C1, C2, C6, C7, C8) is observed. Although the fine structure of the signals assigned to the terminal CH_2 groups of the $(CH_2)_3$ bridge (X-part of an ABX spin system, A and B = ^{31}P, X = ^{13}C) could not be completely resolved, two triplets [^2J(PC)] being observed for the medial CH_2 group.

The presence of two phosphorus atoms in **23** means that the C-atoms C1(3), C4(6), and C7−C9 represent the X-part of ABX spin systems (X = ^{13}C, A and B = ^{31}P; for the numbering scheme for the carbon atoms see Figure 3a). Higher order $^{13}C\{^1H\}$-NMR spectra appearing as doublets of doublets (C1, C3), five line (C9) and six line patterns

Figure 1. (a) Numbering scheme for the carbon atoms in mono- and disubstituted aromatic phosphanes; (b) conformation of the Ph(R)P-group with respect to the plane of the substituted aromatic ring; (c) ^{13}C-NMR spectrum of **8**

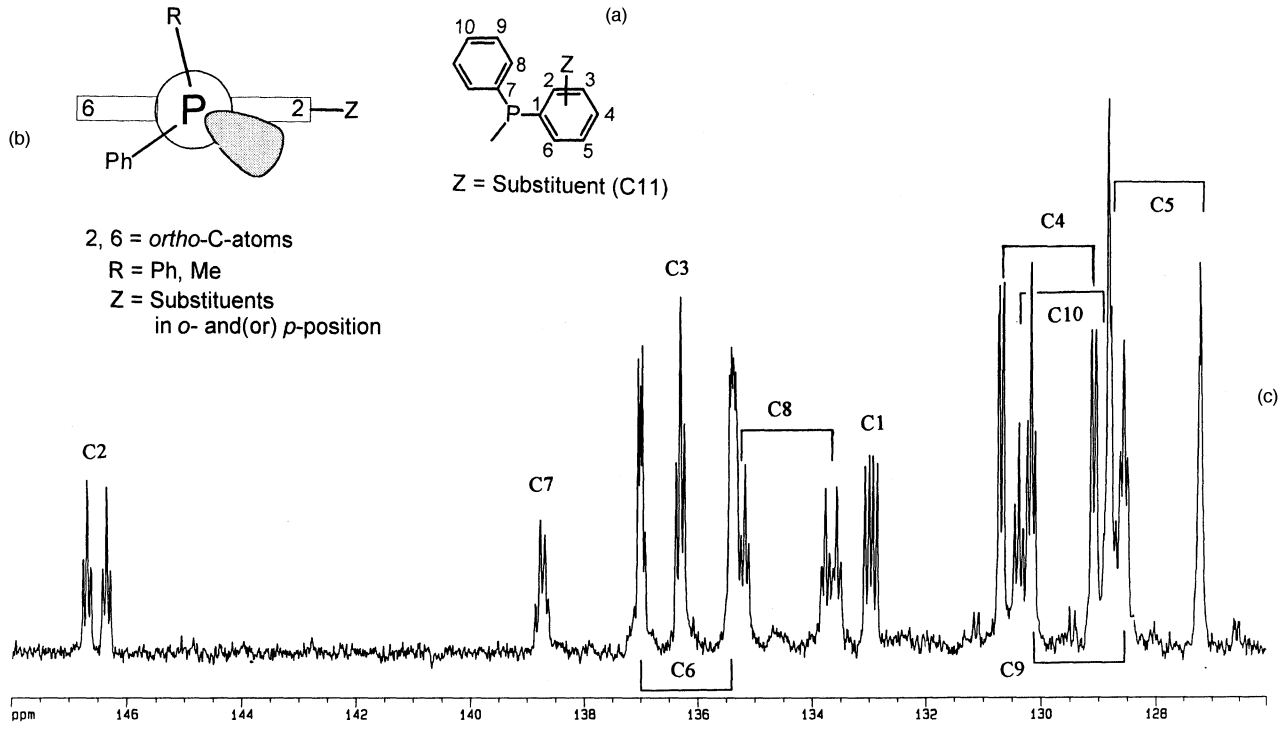
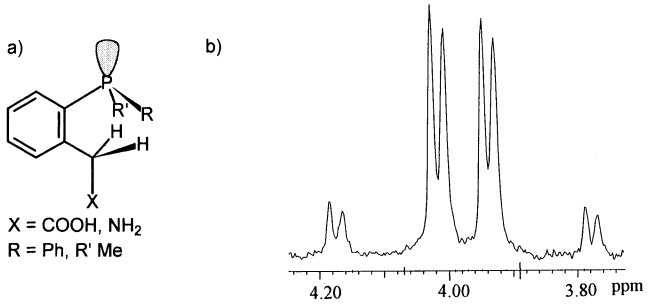


Figure 2. (a) Conformation of the CH_2-X group in **12** and **17**; (b) ^{1}H-NMR spectrum (CH_2-part) of **17**



(C7, C8) are observed (Figure 3b). The analysis of the latter gave a value of around 4.8 Hz for the long range P-P coupling constant [^4J(PP)]. The resonances of C2 and C11 (X-parts of XA_2 spin systems) show first order triplet splitting, while singlets are obtained for C4(6) and C5.

The hydrogen atoms of the CH_2 groups in **12**, **17**, **17a**, **19**, and **19**·HCl are diastereotopic due to the asymmetric substitution at the phosphorus atoms (see Figure 2a). The ^{1}H-NMR spectra of these compounds therefore represent the AB part of an ABX spin system (A and B = ^{1}H, X = ^{31}P) and appear as an eight-line pattern in the cases of **17** (Figure 2b), **17a**, and **19**. The coincidence of lines means that a six-line pattern is observed for **19**·HCl and **12**.

This work was supported by the *Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie* and *the Fonds der Chemischen Industrie*. The *Hoechst AG* is thanked for financial support and generous gifts of chemicals.

Experimental Section

Experimental details are given in part VIII of this series[1]. Phenylphosphane, phenylmethyl- and diphenylphosphane were prepared according to literature methods[26]. 2-, 3-, and 4-Fluorobenzoic acid, 3-fluorophthalic acid, 2- and 4-fluorophenylacetic acid, 2-, 3-, and 4-fluorobenzonitrile, and 2- and 4-fluorobenzylamine were purchased from The Aldrich Chemical Company and used without further purification.

Preparation of **1** *by Phosphanylation of 2-F−C_6H_4−COOK with Ph_2PK:* To 20 ml of a 0.5 M solution of Ph_2PK (10.0 mmol) in THF was added 1.8 g (10.0 mmol) of 2-F−C_6H_4−COOK with stirring and the reaction mixture was heated at 60 °C for 20 h. After extraction with 20 ml of conc. KOH solution the aqueous phase was acidified with conc. HCl until a precipitate formed. The mixture was then extracted with 40 ml of diethyl ether and the extracts were dried over Na_2SO_4. Evaporation of the solvent in vacuo gave **1** as a colorless solid. Yield: 1.97 g (64%). − **1**: $C_{19}H_{15}O_2P$ (306.3): calcd. C 74.50, H 4.94; found C 74.20, H 4.96. − MS: (M^+: *m/z* = 306). − IR: ν(COOH): 1695, 1305 cm^{-1}.

Preparation of **2** *and* **4**−**8**: The lithium salts of the fluorobenzoic acids or 3-fluorophthalic acid were added at ambient temperature to either a THF solution of Ph_2PK or to a suspension of $PhPLi_2$ in THF (obtained by metalation of $PhPH_2$ with *n*BuLi in *n*-hexane in the presence of tetramethylethylenediamine at −40 °C), respectively (see Table 4). After the reaction mixtures were refluxed for 2 h the solvents were removed under reduced pressure (30 °C, 1 mbar). The remaining residues were dissolved in 100 ml of water and filtered through a fine porosity fritted funnel. On acidification of the filtrate the phosphanes precipitated as colorless powders which were further purified by recrystallization from methanol/water mixtures. In the cases of compounds **4** and **8** the filtrates

Figure 3. (a) Numbering scheme for the carbon atoms in **23**; (b) $^{13}C\{^1H\}$-NMR spectrum of **23**

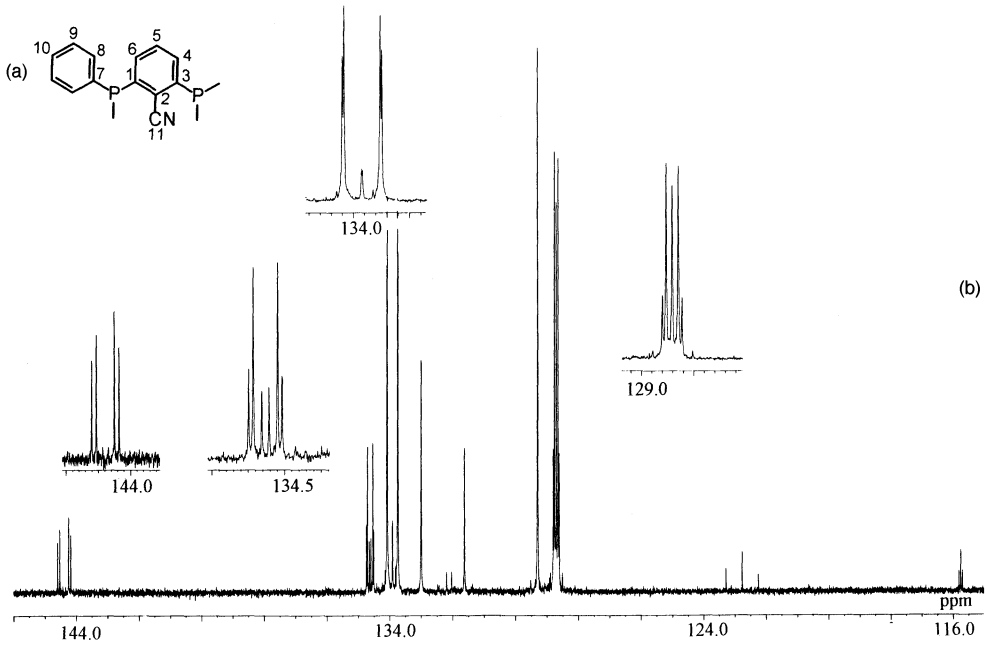


Table 3. Selected ^{1}H-NMR data of **10**−**19**[a]; shifts relative to TMS (int.), coupling constants (in parentheses) in Hz

	P(Me)	CH_2	NH_2	COOH
10		4.12		11.69
11		3.63		
12	1.57 (3.8)[b]	4.10[c] (16.7)[d]		10.74
		3.94[c] (−1.3)[e], −0.2[f]		11.79
13	1.59 (3.1)[b]	3.58		
14		4.05 (1.65)[g]	1.95[h]	
15		3.82	1.61	
16		3.83	2.23	
17	1.59 (4.2)[b]	3.89[c] (14.3)[d]	1.37	
		4.07[c] (−1.73)[e]		
		(−1.94)[f]		
18	1.31 (3.9)[b]	3.55	1.39	
19	5.19[i] (221.3)[j]	3.91[c] (14.4)[d]		
		4.02[c] (0.9)[e,f]		
19·HCl		4.45 (14.1)[d]		
		4.27 (0.3)[e] (−1.9)[f]		

[a] Solvents: $CDCl_3$ (**12**, **14**−**16**, **18**), CD_2Cl_2 (**10**, **13**, **19**), CD_3OD (**17**), [D_6]acetone (**11**). − [b] ^2J(PH). − [c] AB part of ABX spin system. − [d] ^2J(HH) (AB). − [e] ^4J(PH) (AX). − [f] ^4J(PH) (BX). − [g] ^4J(PH). − [h] Broad. − [i] δ (PH). − [j] ^1J(PH).

were extracted with 30 or 50 ml of diethyl ether prior to acidification (reaction conditions and yields are given in Table 4).

2: $C_{19}H_{15}O_2P$ (306.3): calcd. C 74.50, H 4.94; found C 73.81, H 5.19. − MS (M^+: *m/z* = 306). − IR: ν(COOH) = 1695, 1300 cm^{-1}.

4: $C_{20}H_{15}O_4P$ (350.3): calcd. C 68.57, H 4.32; found C 67.83, H 4.64. − MS ($M^+ - H_2O$: *m/z* = 332). − IR: ν(COOH) = 1715, 1280 cm^{-1}.

5: $C_{20}H_{15}O_4P$ (350.3): calcd. C 68.57, H 4.32; found C 66.93, H 4.42. − MS (M^+: *m/z* = 350). − IR: ν(COOH) = 1680, 1300 cm^{-1}.

6: $C_{20}H_{15}O_4P$ (350.3): calcd. C 68.57, H 4.32; found C 68.57, H 4.48. − MS (M^+: *m/z* = 350). − IR: ν(COOH) = 1680, 1300 cm^{-1}.

7: $C_{20}H_{15}O_4P$ (350.3): calcd. C 68.57, H 4.32; found C 68.77, H 4.69. − MS (M^+: *m/z* = 350). − IR: ν(COOH) = 1690, 1295 cm^{-1}.

8: $C_{22}H_{15}O_8P \cdot 4H_2O$ (510.4): calcd. C 51.77, H 4.54; found C 52.24 H 4.33. − MS ($M^+ - 2\,H_2O$: *m/z* = 402). − IR: ν(COOH) = 1715, 1280 cm^{-1}.

Table 4. Syntheses of **2**, **4**−**8**, **10**−**13**

	Ar*F g (mmol)	Phosphide g (mmol)	Solvent ml	Temp. [°C]	Time	Yield g (%)
2	K-3-fluoro-benzoate 1.8 (10)	Ph_2PK 2.24 (10)	THF 30	60	20 h	1.97 (64)
4	Li-3-fluoro-phthalate 2.94 (15)	Ph_2PK 3.36 (15)	THF 30	60	2.5 h	3.7 (70)
5	Li-2-fluoro-benzoate 7.3 (50)	$PhPLi_2$ 3.05 (25)	THF 100	60	5 h	6.3 (72)
6	Li-3-fluoro-benzoate 5.84 (40)	$PhPLi_2$ 2.44 (20)	THF 80	60	6 d	4.3 (61)
7	Li-4-fluoro-benzoate 3.94 (27)	$PhPLi_2$ 1.52 (12.5)	THF 50	20	12 h	3.6 (82)
8	Li-3-fluoro-phthalate 9.8 (50)	$PhPLi_2$ 3.05 (25)	THF 170	60	12 h	8.9 (70)
10	K-2-fluorophenyl-acetate 2.0 (10.4)	Ph_2PK 2.6 (11.4)	DME 30	85	12 h	1.94 (58)
11	K-4-fluorophenyl-acetate 2.0 (10.4)	Ph_2PK 2.6 (11.4)	DME 30	85	12 h	1.8 (54)
12	K-2-fluorophenyl-acetate 2.0 (10.4)	Ph(Me)PK 1.8 (11.4)	DME 30	85	12 h	1.88 (70)
13	K-4-fluorophenyl-acetate 2.18 (11.3)	Ph(Me)PK 2.0 (12.4)	DME 30	85	12 h	1.9 (65)

Preparation of **9**: 1.23 g (32 mmol) of potassium was added to a solution of 3.45 g (31 mmol) of phenylphosphane in 50 ml of THF and the reaction mixture was stirred for 2 h. The reaction mixture was refluxed under nitrogen for an additional 30 min in order to ensure completion of the reaction. Excess potassium was removed by decanting the solution. 3.00 g (15 mmol) of 1,3-dibromopropane was added and the yellow color of the solution disappeared. After

dilution with 30 ml of THF a further equivalent of 1.23 g (32 mmol) of potassium was added and the reaction mixture was again refluxed for 2 h. The lithium salt of 3-fluorophthalic acid was added and the color of the reaction mixture became dark red. After stirring for 12 h at 60−70 °C the color disappeared. All volatile components were then removed under reduced pressure (30 °C, 1 mbar). The residue obtained was dissolved in 200 ml of water and filtered through a fritted funnel. The filtrate was washed with three 50-ml portions of diethyl ether and then acidified with half conc. HCl. The white solid that precipitated was separated by filtration and recystallized from water/methanol. Yield: 4.1 g (41%). − **9**: $C_{31}H_{26}O_8P_2 \cdot 4H_2O$ (660.55): calcd. C 56.37, H 5.19; found C 55.51, H 5.33. − MS ($M^+ - 2\ H_2O$: *m/z* = 552. − IR: ν(COOH) = 1705, 1280 cm^{-1}.

Synthesis of **10**−**13**. − *General Procedure:* To a solution of Ph_2PK or Ph(Me)PK in DME [prepared by metalation of Ph_2PH or Ph(Me)PH with equimolar amounts of potassium] was added potassium 2- or 4-fluorophenyl acetate. The suspensions were refluxed until the yellow color of the potassium phosphides disappeared. The solvent was removed under reduced pressure (20 °C, 0.01 mbar) and, in each case, the solid obtained was dissolved in 50 ml of water. Unreacted phosphane was extracted with dichloromethane. After cooling to about 0 °C, the aqueous phase was acidified with conc. HCl. The phosphanylphenylacetic acids precipitated and were isolated by filtration through a fine porosity fritted funnel. A slurry was obtained by suspending the residue in 50 ml of water and 1 equivalent of KOH was added. The solution formed was filtered, cooled to about 0 °C and acidified with conc. HCl. The precipitate was isolated by filtration and dried in vacuo (20 °C, 0.01 mbar). The amounts of starting materials and yields are given in Table 4.

10: $C_{20}H_{17}O_2P$ (320.3): calcd. C 74.99, H 5.35; found C 74.33, H 5.56. − MS (M^+: *m/z* = 320). − IR: ν(COOH) = 1714 cm^{-1}.

11: $C_{20}H_{17}O_2P$ (320.3): calcd. C 74.99, H 5.35; found C 74.33, H5.49. − MS (M^+: *m/z* = 320). − IR: ν(COOH) = 1736 cm^{-1}.

12: $C_{15}H_{15}O_2P$ (258.3): calcd. C 69.76, H 5.85; found C 68.96, H 5.98. − MS (M^+: *m*/e = 258). − IR ν(COOH) = 1701 cm^{-1}.

13: $C_{15}H_{15}O_2P$ (258.3): calcd. C 69.76, H 5.85; found C 69.08, H 5.89. − MS (M^+: *m/z* = 258). − IR ν(COOH): 1712 cm^{-1}.

Preparation of **14**−**19** *by Phosphanylation of Fluorobenzylamines.* − *General Procedure:* In a typical procedure the fluorobenzylamines were added to a solution of Ph_2PK or Ph(Me)PK in DME with stirring. After heating the reaction mixtures at reflux for 24 h the solvent was evaporated under reduced pressure (20 °C, 0.01 mbar) and the residue obtained was washed with 100 ml of water. The crude products were dried in vacuo and isolated by distillation at 220−240 °C and 10^{-3} mbar. Starting materials, reaction conditions and yields are given in Table 5.

14: $C_{19}H_{18}NP$ (291.4): calcd. C 78.33, H 6.23, N 4.81; found C 77.24, H 6.23, N 4.81. − MS (M^+: *m/z* = 291). − IR: ν_{as}/ν_s-NH_2 = 3376, 3313 cm^{-1}.

15: $C_{19}H_{18}NP$ (291.4): calcd. C 78.33, H 6.23, N 4.81; found C 78.10, H 6.54, N 4.83. − MS (M^+: *m/z* = 291). − IR: ν_{as}/ν_s-NH_2 = 3371, 3298 cm^{-1}.

16: $C_{19}H_{18}NP$ (291.4): calcd. C 78.33, H 6.23, N 4.81; found C 77.33, H 6.46 N 4.51. − MS (M^+: *m/z* = 291). − IR: ν_{as}/ν_s-NH_2 = 3371, 3294 cm^{-1}.

17: $C_{14}H_{16}NP$ (229.3): calcd. C 73.35, H 7.03, N 6.11; found C 72.53, H 7.31, N 6.23. − MS (M^+: *m/z* = 229). − IR: ν_{as}/ν_s-NH_2 = 3356, 3289 cm^{-1}.

18: $C_{14}H_{16}NP$ (229.3): calcd. C 73.35, H 7.03, N 6.11; found C 72.49, H 7.14, N 6.23. − MS (M^+: *m/z* = 229). − IR: ν_{as}/ν_s-NH_2 = 3366, 3304 cm^{-1}.

19: $C_{13}H_{14}NP$ (215.2): calcd. C 72.54, H 6.56, N 6.51; found C 72.38, H 6.67, N 6.29. − MS (M^+: *m/z* = 215). − IR: ν_{as}/ν_s-NH_2 = 3366, 3292 cm^{-1}.

Table 5. Syntheses of **14**−**23** by nucleophilic phosphanylation of Ar*F in DME/THF

	Ar*F(Cl) g (mmol)	Phosphide g (mmol)	Solvent ml	Temp. [°C]	Time	Yield g (%)
14	2-F-benzylamine 3.13 (25)	Ph_2PK[a] 5.6 (25)	DME 50	85	1 d	6.90 (95)
15	3-F-benzylamine 1.25 (10)	Ph_2PK[a] 2.2 (10)	DME 20	85	1 d	1.85 (56)[b]
16	4-F-benzylamine 3.59 (28.7)	Ph_2PK[a] 6.4 (28.7)	DME 30	85	1 d	6.55 (70)[b]
17	2-F-benzylamine 0.98 (7.8)	Ph(Me)PK[a] 1.3 (7.8)	DME 10	85	1 d	1.12 (54)[b]
18	4-F-benzylamine 1.96 (15.7)	Ph(Me)PK[a] 2.5 (15.7)	DME 10	85	1 d	3.02 (84)
19	2-F-benzylamine 9.13 (73)	Ph(H)PK[a] 10.8 (73)	DME 40	85	1 d	7.9 (50)
20	2-F-benzonitrile 1.81 (15)	Ph_2PLi[c] 2.9 (15)	THF 30	−78	15 min	2.65 (62)
21	3-F-benzonitrile 1.39 (11.5)	Ph_2PLi[c] 2.2 (11.5)	THF 30	−78	2 min	2.1 (65)
22	4-Cl-benzonitrile 3.95 (28.7)	Ph_2PK[a] 6.4 (28.7)	DME 30	0	10 h	5.45 (67)
23	2,5-difluoro-benzonitrile 2.83 (20.3)	Ph_2PK[a] 9.13 (40.7)	THF 100	−78	1 min	7.76 (81)

[a] Prepared by reaction of equivalent amounts of Ph_2PH or Ph(Me)PH with potassium (in DME). − [b] Isolated as HCl adducts, for the preparation from the amines see below. − [c] Prepared by reaction of equivalent amounts of Ph_2PH with *n*BuLi (1.6 M solution in *n*-hexane) in stoichiometric ratios in THF.

Synthesis of **20**−**23** *by Phosphanylation of 2- or 3-Fluoro- and 4-Chlorobenzonitrile with Ph_2PM (M = Li, K):* Diphenylphosphane was dissolved in THF and metalated at 0 °C by the addition of the eqivalent amount of *n*BuLi (1.6 M solution in *n*-hexane). The red colored solution of Ph_2PLi was cooled to −78 °C and stoichiometric amounts of 2- or 4-fluorobenzonitrile were added at this temperature. After removal of the solvent in vacuo the oily residue was washed with water and recrystallized from ethanol. For the preparation of **22** and **23**, 4-chlorobenzonitrile or 2,6-difluorobenzonitrile, respectively, were used as starting materials along with Ph_2PK. Ph_2PK was prepared by reaction of equivalent amounts of Ph_2PH and potassium. The workup procedure was the same as that described above. The crude products were recrystallized from methanol. Starting materials, reaction conditions and yields are given in Table 5.

20: $C_{19}H_{14}NP$ (287.3): calcd. C 79.43, H 4.91, N 4.81; found C 79.05, H 4.89, N 4.88. − MS (M^+: *m/z* = 287). − IR: ν(CN) = 2219 cm^{-1}.

21: $C_{19}H_{14}NP$ (287.3): calcd. C 79.43, H 4.91, N 4.81; found C 79.41, H 4.88, N 4.84. − MS (M^+: *m/z* = 287). − IR: ν(CN) = 2225 cm^{-1}.

22: $C_{19}H_{14}NP$ (287.3): calcd. C 79.43, H 4.91, N 4.81; found C 79.02, H 4.84, N 4.86. − MS (M^+: *m/z* = 287). − IR: ν(CN) = 2225 cm^{-1}.

23: $C_{31}H_{23}NP_2$ (471.5): calcd. C 78.97, H 4.92, P 13.14; found C 79.01, H 5.04, P 13.07. − MS (M^+: *m/z* = 471).

Reduction of **20** *and* **21** *with* $LiAlH_4$: To a suspension of 0.38 g (10 mmol) or 0.13 g (3.6 mmol) of $LiAlH_4$ in 80 or 40 ml of THF was added over 15 min a solution of 2.87 g (10 mmol) of **20** or 1.00 g (3.5 mmol) of **21** in 20 or 10 ml of THF. After stirring for 0.5 h at ambient temperature the reaction mixtures were refluxed for 1 h. The precipitate formed on the addition of 20 or 50 ml of water, respectively, was separated by filtration and the solvent was removed in vacuo (20 °C, 0.01 mbar). The remaining crude reaction products were purified by vacuum distillation (220−240 °C, 10^{-3} mbar). Yields: 2.45 g (84%) of **14** and 0.82 g (80%) of **15**.

Protonation of **14** *with HCl:* 0.5 g (1.7 mmol) of diphenylphosphanylbenzylamine (**14**) was dissolved in diethyl ether. An etheral solution of HCl was added until no further precipitate was formed. The solid was filtered off using a coarse porosity fritted funnel and then dried in vacuo (20 °C, 0.1 mbar). Yield: 0.50 g (89%) of **14a**.

14a: $C_{19}H_{19}ClNP$ (327.8): calcd. C 69.62, H 5.84, N 4.27; found C 68.56, H 5.89, N 4.22. − MS (M^+ − HCl: *m*/*z* = 291).

Synthesis of **1**, **3**, **20**−**22** *in the Superbasic Medium. − General Procedure:* Diphenyl- or phenylphosphane were added to a suspension of powdered KOH (88%) in DMSO and the mixtures were stirred for 1 h at ambient temperature. After addition of the appropriate amounts of the fluoroaromatic compounds (see Table 6), the orange to red colored solutions were heated for 70 h at 60−70 °C in the cases of **1** and **3**. The reactions of the fluorobenzonitriles with the phosphanes were complete within a couple of minutes. For the isolation of **1** and **3** the reaction mixtures were first extracted with 200 ml of diethyl ether. After acidification with conc. HCl extraction was repeated with three 75-ml portions of diethyl ether. The organic extracts were washed with 30 ml of water and then dried over $MgSO_4$. The residue obtained after evaporation of the solvents in vacuo was recrystallized from methanol. **20**−**22** were precipitated from the reaction mixtures by addition of 30−40 ml of water and separated by filtration. Further purification was possible by recrystallization from methanol. **1**, **3**, **20**−**22** prepared by this route gave correct analyses. The compounds were identified by NMR spectroscopy (see above). Starting materials, reaction conditions and yields are given in Table 6.

Table 6. Syntheses of **1**, **3**, **20**−**22** by nucleophilic phosphanylation of Ar*F in the superbasic medium DMSO/KOH

	Ar*F(Cl) g (mmol)	Phosphane g (mmol)	DMSO ml	KOH g (mmol)	Temp. [°C]	Time	Yield g (%)
1	2-fluoro-benzoic acid 3.5 (25)	Ph_2PH 4.65 (25)	40	3.83 (60)	20	72 h	3.5 (46)
3	K-4-fluoro-benzoate 4.5 (25)	Ph_2PH 4.80 (25.8)	70	1.9 (30)	55−60	20 h	5.1 (68)
20	2-fluoro-benzonitrile 6.06 (50)	Ph_2PH 9.3 (50)	80	3.83 (60)	20	10 min	11.9 (82)
21	3-fluoro-benzonitrile 1.2 (10)	Ph_2PH 1.86 (10)	40	0.77 (12)	20	10 min	2.4 (82)
22	4-chloro-benzonitrile 1.4 (10)	Ph_2PH 1.86 (10)	50	1.0 (1.5)	20	10 min	2.65 (92)

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