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Water soluble phosphines
VIII. Palladium-catalyzed P–C cross coupling reactions between primary or secondary phosphines and functional aryliodides — a novel synthetic route to water soluble phosphines [1]

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Abstract

Tertiary phosphines Ph_2P–Ar and $PhP(Ar)_2$ containing mono- and disubstituted aromatic ring systems Ar (Ar = C_6H_4–X and C_6H_3–XY; X, Y = Me, OH, NH_2, COOH, COOMe and SO_3Na) are accessible in good yields by Pd(0)-catalyzed cross coupling reactions between diphenylphosphine or phenylphosphine and substituted aryliodides I–C_6H_4–X or I–C_6H_3–XY in organic solvents (dimethylacetamide, acetonitrile, methanol) using organic amines or potassium and sodium acetate as bases. If the primary phosphine is employed in the appropriate stoichiometric ratio, functionalized secondary phosphines, e.g. Ph(H)P–C_6H_4–*p*–SO_3Na, may be obtained selectively.

Keywords: P–C cross coupling; Tertiary and secondary phosphines; Palladium catalysis; Water soluble phosphines; Bromide; Iodide

1. Introduction

The palladium-catalyzed C–C cross coupling reactions (Heck reactions) are an extremely useful synthetic tool in organic chemistry which has been used for arylation and vinylation of a great variety of organic substrates [2]. Very recently, it was shown by Buchwald and coworkers [3a] and Louie and Hartwig [3b] that arylamines are accessible in high yields by Pd(0)-catalyzed C–N cross coupling reaction between secondary amines and various arylbromides employing sodium *tert*-butylate as the base. There are, however, only a very few reports in the literature on the syntheses of phosphine ligands by analogous metal-catalyzed P^{III}–C cross coupling reactions. Using silyl derivatives of primary phosphines $RP(H)SiMe_3$ (R = ^{i}Pr, ^{t}Bu, CEt_3) secondary phosphines RP(H)–Ar–Z (Z = H, Me, Cl, Br, OMe, COOMe, CN) or R(H)P–C(OEt) = CH_2 were obtained in a Stille-type reaction [4] with arylhalides X–Ar–Z (X = Br, I) [5a] or α-bromoalkenylethylether [5b]. Cai et al. [5c] reported a multistage synthesis of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) based on a nickel-catalyzed phosphination of the bistriflate of binaphthol. Arylation of the borane adducts of secondary phosphines, e.g. MenO(H)PhP–BH_3 (Men = l-menthyl), with *o*-iodoanisole in the presence of potassium carbonate, using $PdCl_2$, $Pd(PPh_3)_4$ or $Pd(OAc)_2$ as catalysts, gave optically-pure borane–phosphine complexes MenO(Ar)PhP–BH_3 (Ar = *o*-anisyl) [6].

The synthetic value of these P–C-coupling reactions would be considerably enhanced, however, if the secondary and primary phosphines (and possibly PH_3) could be employed directly instead of the elusive silyl derivatives or the borane complexes. Also, the halides would be much more attractive as arylating agents than the expensive triflates.

In the context of a program for the development of new synthetic routes to water soluble phosphines [7], our primary interest was directed towards P–C cross coupling reactions between aryl halides with polar sub-

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stituents (OH, NH_2, COOH and SO_3M; M = Na, K) and Ph_2PH or $PhPH_2$.

2. Results and discussion

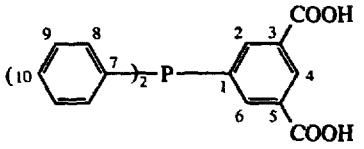
Using diphenylphosphine and phenylphosphine as starting materials, a great variety of tertiary phosphines (**1–18**) could be obtained by palladium-catalyzed cross coupling with mono- or disubstituted arylhalides X–C_6H_4–I (X = *p*-Me, *m*-, *p*-COOH, *o*-COOMe, *p*-OH, *o*-, *m*-, *p*-NH_2) or XYC_6H_3–I (X, Y = *m*-Me_2, *m*-$(COOH)_2$; X = *p*-OH, Y = *m*-COOH) respectively (Table 1). The reactions were carried out in pure organic solvents (DMA, CH_3CN and CH_3OH) (entries 1–7, 9–11, 14–18) or solvent mixtures (CH_3CN/water, entries 8, 12, 13) using organic amines (NEt_3, $EtCy_2N$, $N(^nBu)_3$) or KOAc and NaOAc as bases (Eq. (1)). The P–C coupling reactions were initiated by addition of palladium(II) acetate in most cases. For the cross coupling between *o*- and *m*-H_2N–C_6H_4–I and Ph_2PH or $PhPH_2$ (entries 8, 12, 13), the catalyst used was $Pd(Ph_3P)_4$ [8,9].

$$Ph_2PH + Ar\text{–}I \xrightarrow[\text{cat.}]{\text{base}} Ph_2P\text{–}Ar \qquad (1)$$

1–10

Ar–I: X–C_6H_4–I (X = *p*-Me, *m*-, *p*-COOH, *o*-COOMe, *p*-OH, *o*-, *p*-NH_2);
XY–C_6H_3–I (X = Y = 3,5-Me_2, 3,5-$(COOH)_2$; X = *p*-OH; Y = *m*-COOH)

cat.: Pd(II) acetate, $Pd(Ph_3P)_4$
base: KOAc, NEt_3, NBu_3



The single step syntheses of the phosphines **1** [10a], **3**, **4** [10b] **5** [10c], **8** [11], **9**, **13** [12a] and **10** [12b] according to Eq. (1) are superior to the methods reported in the literature. *o*-Aminophenyldiphenylphosphine (**8**) is of actual interest as a building block for the syntheses of chiral mono and tetradentate PN–hybride donor systems [13a] and has been employed as a ligand in unusual complexes containing the $[M^V = O]^{3+}$ (M = Tc, Re) core [13b]. The salicylic acid derivative **7** represents a novel type of phosphine ligand capable of binding soft and hard transition metals via the Ph_2P donor and the COOH/OH chelate system [14] respectively. Phosphine ligands of type **6** containing 3,5-biscarboxylated aromatic substituents have not been reported before.

The active catalyst for the P–C cross coupling reactions (entries 1–7, 9, 10) according to Eq. (1) is probably formed in an analogous way as reported for the $Pd(OAc)_2/Ph_3P$ system [15], Ph_2PH or the tertiary phosphines Ph_2P–C_6H_4–X, Ph_2P–C_6H_3–XY acting as reductants towards $Pd(OAc)_2$. The secondary phosphine complex $Pd(Ph_2PH)_4$ [16] itself can be excluded as an active catalyst since it is insoluble in any solvent with which it does not react. The Ph_2PH ligand may, how-

Table 1
Palladium-catalyzed P–C cross coupling reactions between Ph_2PH, $PhPH_2$ and aryliodides (bromides)

	Phosphine	X–Ar–I(Br) XY–Ar–I	Catalyst/solvent [a,b]	Base	Time (h)/ Temp. (°C)	Reaction product	Yield (%)
1	Ph_2PH	4-MeC_6H_4I	a/DMA	KOAc	1.5/130	4-Me–C_6H_4–PPh_2 (1)	80
2	Ph_2PH	3,5-$Me_2C_6H_3I$	a/DMA	KOAc	1.5/130	3,5-$Me_2C_6H_3$–PPh_2 (2)	93
3	Ph_2PH	4-HOOC–C_6H_4I	a/CH_3CN	NEt_3	12/80	4-HOOC–C_6H_4–PPh_2 (3)	73
4	Ph_2PH	3-HOOC–C_6H_4I	a/CH_3CN	NEt_3	12/80	3-HOOC–C_6H_4–PPh_2 (4)	58
4a	Ph_2PH	3-HOOC–C_6H_4Br	a/DMA	NBu_3	170/125	3-HOOC–C_6H_4–PPh_2 (4)	76
5	Ph_2PH	2-MeOOC–C_6H_4I	a/CH_3CN	NEt_3	4/85	2-MeOOC–C_6H_4–PPh_2 (5)	72
6	Ph_2PH	3,5-$(COOH)_2$–C_6H_3–I	a/CH_3CN	NEt_3	12/90	3,5-$(COOH)_2$–C_6H_3–PPh_2 (6)	77
7	Ph_2PH	5-Iodosalicylic acid	a/CH_3CN	NEt_3	12/80	3-HOOC–4-HO–C_6H_3–PPh_2 (7)	66
8	Ph_2PH	2-H_2N–C_6H_4I	b/CH_3CN/H_2O	NEt_3	34/80	2-H_2N–C_6H_4–PPh_2 (8)	62
9	Ph_2PH	4-H_2N–C_6H_4I	a/DMA	KOAc	3/130	4-H_2N–C_6H_4–PPh_2 (9)	98
10	Ph_2PH	4-HO–C_6H_4I	a/DMA	KOAc	1/130	4-HO–C_6H_4–PPh_2 (10)	67
11	$PhPH_2$	3,5-$Me_2C_6H_3I$	a/DMA	Cy_2NEt	72/130	$(3,5\text{-}Me_2C_6H_3)_2PPh$ (11)	56
12	$PhPH_2$	2-H_2N–C_6H_4I	b/CH_3CN/H_2O	NEt_3	14/80	$(2\text{-}H_2N\text{-}C_6H_4)_2PPh$ (12)	80 [c]
13	$PhPH_2$	3-H_2N–C_6H_4I	b/CH_3CN/H_2O	NEt_3	70/75	$(3\text{-}H_2N\text{-}C_6H_4)_2PPh$ (13)	73 [c]
14	$PhPH_2$	4-HOOC–C_6H_4I	a/CH_3CN	NEt_3	70/85	$(4\text{-HOOC-}C_6H_4)_2PPh$ (14)	49
15	$PhPH_2$	3-HOOC–C_6H_4I	a/CH_3CN	NEt_3	72/85	$(3\text{-HOOC-}C_6H_4)_2PPh$ (15)	60
16	$PhPH_2$	4-NaO_3S–C_6H_4I	b/CH_3OH	NEt_3	12/70	$(4\text{-}NaO_3S\text{-}C_6H_4)PPhH$ (16)	78
17	$PhPH_2$	4-NaO_3S–C_6H_4I	b/CH_3OH	NEt_3		$(4\text{-}NaO_3S\text{-}C_6H_4)_2PPh$ (17)	3
18	Ph_2PH	2,6-$Br_2C_5NH_3$	a/DMA	NaOAc	2/130	2,6-$(Ph_2P)_2C_5NH_3$ (18)	67

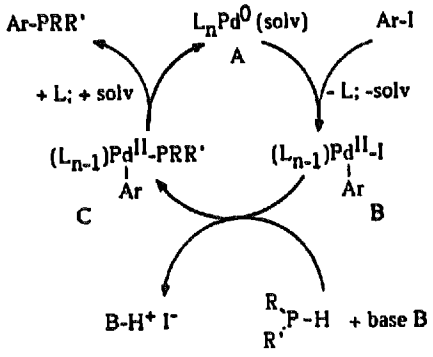
[a] $Pd(OAc)_2$, 0.05–0.6 mol%. [b] $Pd(Ph_3P)_4$, 1–2 mol%. [c] Isolated as anilinium salt.

ever, be replaced by various donor molecules giving soluble mixed ligand Pd(0) complexes, e.g. **A**.

The formation of the tertiary phosphines $Ph_2P-C_6H_4-X$ or $Ph_2P-C_6H_3-XY$ according to Eq. (1) may be explained by a reaction sequence (Scheme 1) analogous to that proposed for the palladium-catalyzed amination of arylbromides [3]. Oxidative addition of the aryliodides $I-C_6H_4-X$ or $I-C_6H_3-XY$ to the catalytically active palladium(0) species, e.g. **A**, yields the intermediate **B**, which on base-assisted nucleophilic replacement of the iodine ligand by the diphenylphosphido group gives the $Ph_2P-Pd(II)-C_6H_4-X$ ($Ph_2P-Pd(II)-C_6H_3-XY$) intermediate **C**. Herrmann et al. [17] demonstrated that the iodine ligands in complexes of type **B** may be replaced by other nucleophiles like Cl^- on treatment with the corresponding ammonium salts. e.g. $nBu_4N^+Cl^-$. The tertiary phosphines $Ph_2P-Ar-X(XY)$ are finally formed in a reductive elimination step from **C**, the catalyst (**A**) being obtained back again.

The large excess of the phosphine ligands (Ph_2PH and $PhPH_2$, intermediates and the products) present in the reaction mixtures obviously does not lead to a 'poisoning' [5c] of the catalyst. As in case of the hydrogenation of α,β-unsaturated aldehydes [18a] and the hydroformylation of 1-hexene [18b] or propene [18c], the catalysts $RuCl_3$/TPPTS (TPPTS = tris(*m*-sulphonatophenyl)phosphine) or $HRh(I)(CO)L_3$ (L = Ph_3P, TPPTS) are not deactivated by excess phosphine ligand. At higher temperatures the catalytically active species are created by ligand dissociation from the coordinatively saturated complexes. Catalyst degradation by P–C cleavage reactions [18d] may be retarded by protective complexation of the metal by excess phosphine.

Arylation of phenylphosphine with aryliodides $X-C_6H_4-I$ (X = *o*-, *m*-NH_2, *m*-, *p*-HOOC, *p*-NaO_3S) or $XY-C_6H_3-I$ (X, Y = *m*-Me_2) proceeds stepwise, the secondary phosphines $Ph(H)P-C_6H_4-X$ or $Ph(H)P-C_6H_3-XY$ being formed initially (Eq. (2a)) as indicated



R, R' = H, Ph
Ar-I = X-C_6H_4-I or XY-C_6H_3-I
L = phosphine ligand
solv = solvent (base)

Scheme 1.

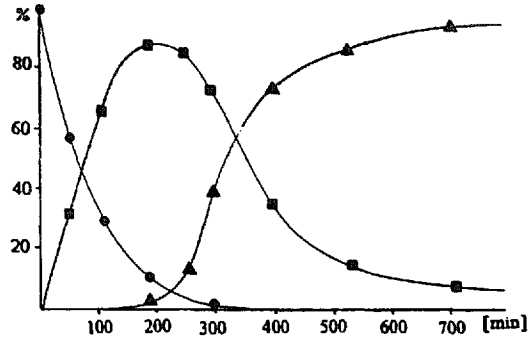


Fig. 1. Concentration–time diagram for the reaction $PhPH_2$/2-$NH_2-C_6H_4-I$ (entry 12, Table 1): ●, $PhPH_2$; ■, 2-$NH_2-C_6H_4-P(H)Ph$; ▲ $(2-NH_2-C_6H_4)_2PPh$.

by the concentration–time profile (Fig. 1) for the reaction between $PhPH_2$ and *o*-$H_2N-C_6H_4-I$. The intermediate secondary phosphines have been identified by their $^{31}P\{^1H\}$ NMR data (δP-values, coupling constants $^1J(P-H)$) [10a,19]. Further reaction of Ph(H)P–Ar with I–Ar (Ar = $I-C_6H_4-X$ or $I-C_6H_3-XY$) leads to the tertiary derivatives (Eq. (2b)).

$$PhPH_2 + Ar-I \xrightarrow[\text{cat.}]{\text{base}} Ph-P(Ar)(H) \qquad (2a)$$

11a–15a, 16, 17a

$$Ph-P(Ar)(H) + ArI \xrightarrow[\text{cat.}]{\text{base}} Ph-P(Ar)(Ar) \qquad (2b)$$

11–15, 17

Ar: X–Ar–I (X = *o*-, *m*-NH_2, *m*-, *p*-COOH, *p*-SO_3Na)
XY–Ar–I (X = Y = Me)
cat.: Pd(II) acetate, $Pd(Ph_3P)_4$
base: NEt_3, $NEtCy_2$

The catalysts employed for the $PhPH_2$ arylations were either $Pd(OAc)_2$ (entries 11, 14, 15) or $Pd(Ph_3P)_4$ (entries 12, 13, 16, 17). Organic amines (NEt_3 or Cy_2NEt) were used as bases in pure organic solvents (DMA, CH_3CN, CH_3OH) or solvent mixtures (CH_3CN/H_2O). Using the Pd-catalyzed P–C coupling reaction, according to Eqs. (2a) and (2b), the bis(aminophenyl)phosphines **12** and **13** are accessible in fair yields. They are of great potential interest as starting materials for the syntheses of cationic water soluble phosphine ligands [20a]. The secondary phosphine **16** with a monosulphonated phenyl group could be obtained by selective arylation of $PhPH_2$ with *p*-I–$C_6H_4-SO_3Na$ in high yields (entries 16, 17), only small quantities of the tertiary derivative **17** being formed as a side product. **16** represents the first member of a series of water soluble derivatives of Ph_2PH with increasing degree of sulphonation including $Ph(H)P-C_6H_3-2,4-(SO_3K)_2$ [20b] and $HP[C_6H_3-2,4-(SO_3K)_2]_2$ [7a,d].

In some cases (syntheses of **14** and **15**) the arylation

of $PhPH_2$ according to Eqs. (2a) and (2b) ceases after a short time because the required soluble catalyst decomposes. The arylation could be restarted by addition of more $Pd(OAc)_2$ (0.6 mol%) to the reaction mixture.

The phosphine ligands obtained by the P–C-coupling reactions according to Eqs. (1) and (2) have been identified by elemental analyses, mass spectra and ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. The expected number of $^{13}C\{^1H\}$ NMR signals have been observed in all cases. The numbering scheme for the carbon atoms, as indicated for **6** in Eq. (1), is used for **1–17** throughout in the Experimental part. Based upon intensity arguments, DEPT spectra and comparison of the δC-values and $^nJ(P-C)$ coupling constants ($n = 1-4$) with relevant NMR data of reference compounds, e.g. Ph_3P [21a], $(4\text{-}SO_3K\text{-}C_6H_4)_3P$ [7a], $(3\text{-}NH_2\text{-}C_6H_4)_3P$ and $(2\text{-}NH_2\text{-}C_6H_4)_3P$ [20a], the $^{13}C\{^1H\}$ NMR signals of **1–17** could be assigned. Using appropriate substituent parameters, the assignments of the carbon atoms could be substantiated by increment calculation [21b] of the chemical shifts δC.

All reactions summarized in Table 1 are metal-catalyzed. The starting materials did not react under the conditions given there in the absence of the palladium catalyst, as shown by separate experiments. For the arylation of Ph_2PH with $2\text{-}MeOOC\text{-}C_6H_4\text{-}I$ (entry 5), it was shown that the rate of reaction is dependent on the catalyst concentration (see Fig. 2). It should be mentioned that $3,5\text{-}Me_2C_6H_3\text{-}PPh_2$ (**2**, entry 2) is also formed in the absence of the palladium catalyst from 3,5-dimethyliodobenzene and Ph_2PH in DMA using KOAc as a base. The non-catalyzed reaction proceeds, however, at a very low rate.

P–C coupling reactions between $PhPH_2$ or Ph_2PH and arylbromides, like $p\text{-}Br\text{-}C_6H_4\text{-}SO_3Na$ and $m\text{-}Br\text{-}C_6H_4\text{-}COOH$ (entry 4a, Eq. (3)), under the conditions summarized in Table 1, proceed much slower than those

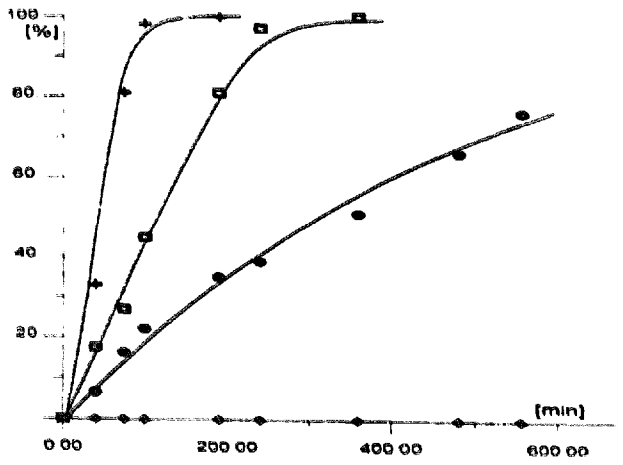
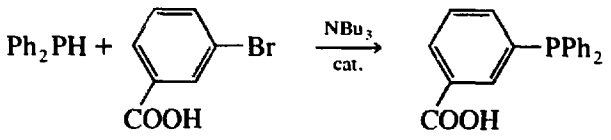


Fig. 2. Dependence of the reaction rate on catalyst concentration ($Pd(OAc)_2$) for the $Ph_2PH/2\text{-}MeOOC\text{-}C_6H_4\text{-}I$ reaction (entry 5, Table 1): +, 0.2; □, 0.1; ●, 0.05 mol% catalyst; ◇, without catalyst.

with the corresponding iodo analogs. 2,6-dibromopyridine, however, containing activated C–Br bonds, reacts with Ph_2PH in a straightforward manner yielding the bisphosphine $2,6\text{-}(Ph_2P)_2\text{-}C_5NH_3$ [22] (Eq. (4)).



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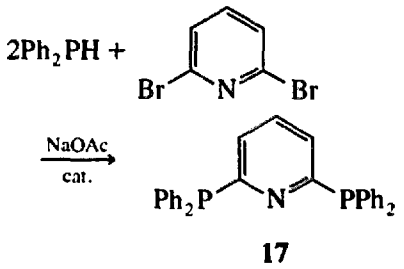
cat.: $Pd(OAc)_2$ (3)



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cat.: $Pd(OAc)_2$ (4)

Investigations concerning the reaction mechanism of the arylation of secondary and primary phosphines (Eqs. (1) and (2)) and the development of more active catalysts for P–C cross coupling reactions with arylbromides are in progress.

3. Experimental section

$PhPH_2$ [23], Ph_2PH [24], $p\text{-}I\text{-}C_6H_4\text{-}SO_3Na$ [25], $Pd(Ph_3P)_4$ [26] were prepared according to literature methods. Starting materials and products were characterized by ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC400 or a Jeol FX90 Q Fourier transform spectrometer. Mass spectra were obtained on a Varian MAT 311A. The palladium(II) acetate catalyst was employed as a stock solution prepared from $Pd(OAc)_2$ in degassed DMA (10 mmol dm^{-3}) and stored in a refrigerator at −30°C in some cases (entries 1, 2, 11, 18).

3.1. General procedure for the preparation of 1, 2, 9, and 10

To a solution of 50 mmol of the iodobenzene derivatives *p*-iodotoluene (10.90 g), 3,5-dimethyliodobenzene (11.60 g), *p*-iodoaniline (10.95 g) or *p*-iodophenol (11.00 g) in 50 ml dimethylacetamide (DMA) 5.98 g (60 mmol) potassium acetate and 11.2 mg (0.05 mmol) Pd(II) acetate were added. The suspension obtained was degassed in vacuo. After addition of 9.31 g (50 mmol) diphenylphosphine the mixtures were heated for 1–3 h until the $^{31}P\{^1H\}$ NMR spectroscopic reaction control indicated complete consumption of the secondary phos-

phine. The reaction mixtures were poured into 250 ml of water and the products separated were dissolved in 100 ml CH_2Cl_2. The CH_2Cl_2 solutions were washed with water (3 × 30 ml), dried over Na_2SO_4 and evaporated in vacuo. Yields: 11.05 g (80%) **1**, 13.50 g (93%) **2**, 13.58 g (98%) **9**, 9.32 g (67%) **10**.

1. $^{13}C\{^1H\}$ NMR (d_6-acetone, δ, ppm): 140.2 (s, C4), 139.1 (d, $J = 11.8$ Hz, C7), 135.2 (d, $J = 20.1$ Hz, C2/6), 134.8 (d, $J = 19.5$ Hz, C8), 130.8 (d, $J = 7.3$ Hz, C3/5), 130.0 (s, C10), 129.9 (d, $J = 7.5$ Hz, C9), C1 resonance superimposed by signal of C2/6 and C8, 21.0 (s, C11); $^{31}P\{^1H\}$ NMR (CD_3OD, δ, ppm): −3.9.

2. Found: C, 82.89; H, 6.70. $C_{20}H_{19}P$ (290.3). Calc.: C, 82.74; H, 6.60%. ^1H NMR (C_6D_6, 250 MHz, δ, ppm): 2.00 (s, 6 H), 6.6–7.6 (m, 13 H); $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 138.9 (d, $J = 12.4$ Hz, C7), 138.7 (d, $J = 7.3$ Hz, C3/5), 138.0 (d, $J = 11.5$ Hz, C1), 134.6 (d, $J = 19.6$ Hz, C8), 132.6 (d, $J = 19.9$ Hz, C2/6), 131.4 (s, C4), 129.3 (d, $J = 6.6$ Hz, C9), 129.2 (s, C10), 21.7 (s, C11/12); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −1.5. MS: $m/e = 290$ [M^+].

9. $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 147.3 (s, C4), 138.1 (d, $J = 10.8$ Hz, C7), 135.4 (d, $J = 21.6$ Hz, C2/6), 133.0 (d, $J = 18.8$ Hz, C8), 128.1 (d, $J = 6.7$ Hz, C9), 128.0 (s, C10), 123.5 (d, $J = 6.2$ Hz, C1), 114.8 (d, $J = 8.4$ Hz, C3/5); $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −7.8.

10. Found: C, 77.58; H, 5.36. $C_{18}H_{15}OP$ (278.3). Calc.: C, 77.68; H 5.43%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 156.8 (s, C4), 137.3 (d, $J = 8.9$ Hz, C7), 135.6 (d, $J = 21.2$ Hz, C2/6), 133.2 (d, $J = 18.9$ Hz, C8), 128.3 (d, $J = 6.8$ Hz, C9), 128.4 (s, C10), 126.7 (d, $J = 6.1$ Hz, C1), 115.9 (d, $J = 8.3$ Hz, C3/5); $^{31}P\{^1H\}$ NMR (CD_3OD, δ, ppm): −4.7.

3.2. Preparation of 11

3,5-Dimethyliodobenzene (8.43 g; 36.3 mmol) and 7.61 g (36.6 mmol) ethyldicyclohexylamine were dissolved in 20 ml DMA together with 7.2 mg (0.03 mmol) Pd(II) acetate. After the solution was degassed in vacuo, 2.0 g (18.1 mmol) phenylphosphine were added and the reaction mixture was heated to 130°C. After 72 h it was cooled and poured into 200 ml of water. The phosphine separated was dissolved in 100 ml petrol ether 40/60. The organic phase was washed with 3 × 20 ml dilute HBr (5%) and dried over Na_2SO_4. **11** was obtained as cream-white powder after removal of the solvent in vacuo. Yield: 3.24 g (56%).

Found: C, 83.00; H, 7.32. $C_{22}H_{23}P$ (318.4). Calc.: C, 82.99; H, 7.28%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 137.7 (d, $J = 7.1$ Hz, C3/5), 137.6 (d, $J = 10.6$ Hz, C7), 136.9 (d, $J = 10.4$ Hz, C1), 133.6 (d, $J = 19.4$ Hz, C8), 131.4 (d, $J = 19.7$ Hz, C2/6), 130.4 (s, C4), 128.3 (s, C10), 128.2 (d, $J = 8.0$ Hz, C9), 21.2 (s, C11/12); $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −3.5. MS: $m/e = 318$ [M^+].

3.3. Preparation of 3, 4, 5, 6 and 7

1.96 g (7.9 mmol) *p*- or *m*-iodobenzoic acid, 2.09 g (7.9 mmol) 5-iodosalicylic acid or 7.84 g (26.9 mmol) 5-iodoisophthalic acid were added together with 1.60 g (16 mmol) or 8.15 g (81.0 mmol) NEt_3 respectively, to 30 ml (60 ml) acetonitrile. After addition of 2.0 mg (0.009 mmol) or 3.0 mg (0.013 mmol) palladium(II) acetate and 1.47 g (7.9 mmol) or 5.0 g (26.9 mmol) Ph_2PH, the intensely brown or orange-red coloured reaction mixture was heated to 85°C for 12 h. For the isolation of **3**, **4** and **7** all volatiles were removed in vacuo and the residue obtained was dissolved in 20 ml of water. After addition of 1.06 g (16 mmol) KOH, the solution was extracted with 3 × 30 ml diethyl ether. The aqueous solution was acidified with 2 N HCl and again extracted with 3 × 30 ml ether. The collected ethereal phases were washed with water (20 ml), dried over $MgSO_4$ and evaporated to dryness. The residues were recrystallized from methanol–water mixtures. Yields: 1.76 g (73%) **3**, 1.40 g (58%) **4**, 1.69 g (66%) **7**.

In the case of **6**, 4.6 ml (55 mmol) conc. HCl were added to the reaction mixture and the solvent was removed in vacuo (1 mbar, 25°C). The residue was washed twice with 10 ml hot 0.5 N HCl and recrystallized from a 3:2 ethanol–water mixture. Yield: 7.25 g (77%).

The phosphine ligand **4** was also obtained by reacting 3.18 g (15.8 mmol) 3-bromobenzoic acid with 1.47 g (7.9 mmol) Ph_2PH in 30 ml DMA after addition of 2.0 mg (0.009 mmol) $Pd(OAc)_2$ for 7 days at 125°C. Using the workup procedure as above, 1.83 g (76%) **4** were obtained.

For the preparation of **5** a solution of 7.04 g (26.9 mmol) iodomethylbenzoate, 2.73 g (27.0 mmol) NEt_3 and 5.0 g (26.9 mmol) diphenylphosphine in 60 ml acetonitrile was heated to 85°C and charged with 3.0 mg (0.013 mmol) palladium acetate. After 4 h stirring, all volatiles were removed in vacuo (20°C, 0.01 mbar). The remaining residue was treated with 250 ml of a 1 : 1 ether–water mixture and the ethereal phase was separated. After evaporation of the solvent, **5** was obtained as a colourless powder. Yield: 6.23 g (72%).

3. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 167.6 (s, C11), 143.5 (d, $J = 14.2$ Hz, C1), 136.4 (d, $J = 10.1$ Hz, C7), 134.1 (d, $J = 20.2$ Hz, C8), 133.5 (d, $J = 18.2$ Hz, C2/6), 131.6 (s, C4), 129.9 (s, C10), 129.9 (d, $J = 6.1$ Hz, C3/5) 129.5 (d, $J = 7.1$ Hz, C9); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −4.7; MS: $m/e = 306$ [M^+].

4. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 167.5 (s, C11), 138.3 (d, $J = 13.2$ Hz, C1), 137.9 (d, $J = 20.2$ Hz, C6), 136.7 (d, $J = 11.0$ Hz, C7), 134.2 (d, $J = 19.2$ Hz, C2), 133.9 (d, $J = 20.2$ Hz, C8), 131.8 (d, $J = 6.1$ Hz, C3), 130.4 (s, C4), 129.8 (s, C10), 129.6 (d, $J = 7.1$ Hz, C5), 129.5 (d, $J = 7.0$ Hz, C9); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −5.3; MS: $m/e = 306$ [M^+].

5. Found: C, 74.85; H, 5.43. $C_{20}H_{17}O_2P$ (320.3). Calc.: C, 74.99; H, 5.35%. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 167.0 (d, $J = 2.0$ Hz, C11), 140.7 (d, $J = 27.3$ Hz, C1), 138.2 (d, $J = 11.1$ Hz, C7), 134.7 (s, C2), 134.5 (s, C6), 134.1 (d, $J = 20.2$ Hz, C8), 132.1 (s, C5), 130.9 (d, $J = 2.0$ Hz, C3), 128.9 (s, C10), 128.7 (d, $J = 7.1$ Hz, C9), 128.4 (s, C4), 52.2 (s, C12); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ ppm): −4.8; MS: $m/e =$ 320 [M^+].

6. Found: C, 67.43; H, 5.32. $C_{20}H_{15}O_4P$ (350.3). Calc.: C, 68.57; H, 4.32%. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 166.9 (s, C11), 139.7 (d, $J = 15.2$ Hz, C1), 137.9 (d, $J = 19.2$ Hz, C2/6), 136.1 (d, $J = 11.1$ Hz, C 7), 134.1 (d, $J = 20.2$ Hz, C8), 132.3 (d, $J = 6.1$ Hz, C3/5), 131.0 (s, C4), 130.0 (s, C10), 129.6 (d, $J = 7.1$ Hz, C9); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −5.3. MS: $m/e = 350$ [M^+].

7. Found: C, 71.13; H, 4.69; P, 9.77. $C_{19}H_{15}O_3P$ (322.3). Calc.: C, 70.81; H, 4.69; P, 9.61%. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 172.0 (s, C11), 162.6 (s, C4), 141.0 (d, $J = 19.2$ Hz, C6), 137.5 (d, $J = 11.1$ Hz, C7), 136.6 (d, $J = 24.3$ Hz, C2), 133.6 (d, $J = 19.2$ Hz, C8), 129.5 (s, C10), 129.3 (d, $J = 7.1$ Hz, C9), 126.6 (d, $J = 10.1$ Hz, C1), 118.6 (d, $J = 6.6$ Hz, C5), 114.3 (d, $J = 9.1$ Hz, C3); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −6.6; MS: $m/e = 322$ [M^+].

3.4. Synthesis of 8, 12 and 13

To a solution of 1.17 g (10.6 mmol) or 1.37 g (12.4 mmol) phenylphosphine or 2.22 g (11.9 mmol) diphenylphosphine respectively, the solutions of 4.65 g (21.3 mmol) *o*-iodoaniline, 5.43 g (24.8 mmol) *m*-iodoaniline or 2.61 g (11.9 mmol) *o*-iodoaniline respectively, in 30 ml acetonitrile are added together with equimolar amounts of triethylamine (2.15 g (21.3 mmol); 2.51 g (24.8 mmol); 1.21 g (11.9 mmol)). The reaction mixtures were heated to reflux and charged with the solution of the catalyst $Pd(Ph_3P)_4$ (0.23 g (0.21 mmol), 0.31 g (0.27 mmol) or 0.14 g (0.12 mmol) respectively) in 10 ml acetonitrile. 10 ml of water was added to the reaction mixture. After 34 h (**8**), 14 h (**12**) or 70 h (**13**) the solvents were removed in vacuo (25°C, 0.01 mbar) and the remaining residue was dissolved in 20 ml of a 1:1 water–CH_2Cl_2 mixture. The organic phase was separated and the solvent removed in vacuo. **8**, **12** and **13** were obtained as light-brown coloured solids.

For a further purification, the aminophenylphosphines **12** and **13** were transformed into the corresponding HCl adducts. Thus **12** and **13**, dissolved in 30 ml THF, were treated with 1.65 M ethereal solutions of HCl (12 or 15 ml respectively). The precipitate formed was collected by filtration, washed with 20 ml of ether and dried in vacuo (25°C, 0.01 mbar) yielding **13** · 2HCl as an off-white powder. Free aminophenylphosphine **12** was obtained by addition of 1.1 g (19.6 mmol) KOH to the solution of **12** · 2HCl in a 40 ml 1:1 mixture of water–CH_2Cl_2. The organic layer was separated and evaporated to dryness in vacuo (25°C, 0.01 mbar) leaving **12** as a white powder. Yields: 2.05 g (62%) **8**, 2.62 g (80%) **12** · H_2O, 3.62 g (73%) **13** · 2HCl · $2H_2O$.

8. $^{13}C\{^1H\}$ NMR (CD_3OD, δ, ppm): 150.7 (d, $J =$ 20.4 Hz, C2), 136.0 (d, $J = 6.1$ Hz., C7), 134.0 (s, C6), 133.5 (d, $J = 19.3$ Hz, C8), 130.2 (s, C4), 128.6 (s, C10), 128.3 (d, $J = 7.1$ Hz, C9), 119.1 (d, $J = 9.2$ Hz, C1), 118.1 (s, C5), 115.4 (d, $J = 3.1$ Hz, C3); $^{31}P\{^1H\}$ NMR (CD_3OD, δ, ppm): −17.6; MS: $m/e = 277$ [M^+].

12. Found: C, 69.81; H, 6.35. $C_{18}H_{17}N_2P \cdot H_2O$ (310.3). Calc.: C, 69.67; H, 6.17%. $^{13}C\{^1H\}$ NMR (CD_3OD, δ, ppm): 150.4 (d, $J = 20.3$ Hz, C2), 134.2 (d, $J = 5.1$ Hz, C7), 133.9 ($J = 2.0$ Hz, C6), 133.8 (d, $J = 19.3$ Hz, C8), 130.4 (s, C4), 128.9 (s, C10), 128.6 (d, $J = 7.1$ Hz, C9), 118.6 ($J = 2.0$ Hz, C5), 117.5 (d, $J = 6.1$ Hz, C1), 115.6 (d, $J = 2.1$ Hz, C3); $^{31}P\{^1H\}$ NMR (CD_3OD, δ, ppm): −33.9; MS: $m/e = 292$ [M^+].

13. Found: C, 53.94; H, 6.01. $C_{18}H_{17}N_2P \cdot 2HCl \cdot 2H_2O$ (401.3). Calc.: C, 53.88; H 5.77%. $^{13}C\{^1H\}$ NMR (CD_3OD, δ, ppm): 139.8 (d, $J = 15.3$ Hz, C1), 135.1 (s, C7), 134.0 (d, $J = 22.4$ Hz, C8), 133.9 (d, $J = 20.4$ Hz, C6), 131.6 (d, $J = 6.1$ Hz, C3), 130.4 (d, $J = 7.1$ Hz, C5), 129.7 (s, C10), 129.0 (d, $J = 7.1$ Hz, C9), 127.7 (d, $J = 18.3$ Hz, C2), 123.9 (s, C4); $^{31}P\{^1H\}$ NMR (CD_3OD, δ, ppm): −0.8; MS: $m/e = 292$ [M^+].

3.5. Synthesis of 14 and 15

To a solution of 6.0 g (24.2 mmol) *p*- or *m*-iodobenzoic acid and 5.0 g (50.0 mmol) NEt_3, 8.1 mg (0.04 mmol) palladium(II) acetate in 70.0 ml acetonitrile was added. Upon addition of 1.33 g (12.0 mmol) $PhPH_2$ small amounts of a black precipitate were formed. The reaction mixtures were heated to 85°C until all of the $PhPH_2$ had been consumed, as indicated by $^{31}P\{^1H\}$ NMR spectroscopic control. Using a workup procedure as above (see preparation of **3–7**) **14** and **15** were obtained. Yields: 2.05 g (49%) **14**, 2.51 g (60%) **15**.

14. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 167.6 (s, C11), 142.6 (d, $J = 14.2$ Hz, C1), 135.6 (d, $J = 10.1$ Hz, C7), 134.4 (d, $J = 20.2$ Hz, C8), 133.8 (d, $J = 19.2$ Hz, C2/6), 131.9 (s, C4), 130.2 (s, C10), 130.0 (d, $J = 7.1$ Hz, C3/5), 129.6 (d, $J = 8.1$ Hz, C9); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −4.8; MS: $m/e = 350$ [M^+].

15. $^{13}C\{^1H\}$ NMR (d_6-DMSO, δ, ppm): 167.4 (s, C11), 138.0 (d, $J = 19.2$ Hz, C6), 137.7 (d, $J = 13.1$ Hz, C1), 136.1 (d, $J = 11.1$ Hz, C7), 134.4 (d, $J = 20.2$ Hz, C2), 134.0 (d, $J = 20.2$ Hz, C8), 132.0 (d, $J = 6.1$ Hz, C3), 130.6 (s, C4), 130.0 (s, C10), 129.8 (d, $J = 7.1$ Hz, C5), 129.6 (d, $J = 7.1$ Hz, C9); $^{31}P\{^1H\}$ NMR (d_6-DMSO, δ, ppm): −5.3; MS: $m/e = 350$ [M^+].

3.6. Preparation of 16 and 17

To a solution of 48.6 g (0.15 mol) p-I–C_6H_4–SO_3Na, 18.2 g (0.18 mol) NEt_3 and 16.5 g (0.15 mol) $PhPH_2$ in 300 ml of methanol, 3.5 g (3.0 mmol) $Pd(Ph_3P)_4$ were added. The reaction mixture was heated to reflux for 12 h. The solvent was removed in vacuo and the remaining residue washed with CH_2Cl_2 (2 × 200 ml) and methanol (50 ml). **16** was obtained as a cream coloured powder, containing small amounts (ca. 3%) of the tertiary phosphine **17**. Yield: 36.0 g (78%) **16**.

16. Found: C, 46.63; H, 3.54; P, 9.42. $C_{12}H_{10}NaO_3PS \cdot H_2O$ (306.3). Calc.: C, 47.06; H, 3.95; P, 10.11%. ^1H NMR (d_6-DMSO, 400 MHz): 7.1–8.1 (m); 3.34 (d, $^1J(PH) = 223$ Hz); $^{13}C\{^1H\}$ NMR (D_2O, δ, ppm): 143.0 (s, C4), 138.2 (s, C1); 134.3 (d, $J = 16.7$ Hz, C2/6), 133.6 (d, $J = 15.2$ Hz, C8), 129.2 (s, C10), 129.0 (d, $J = 6.3$ Hz, C9), 127.3 (s, C7), 125.8 (d, $J = 6.0$ Hz, C3/5); $^{31}P\{^1H\}$ NMR (D_2O, δ, ppm): −41.4 (t, $^1J(PD) = 26.2$ Hz); ^{31}P NMR (d_6-DMSO–H_2O): −39.9 (d, $^1J(PH) = 229$ Hz).

3.7. Synthesis of 18

The suspension of 2.37 g (10.0 mmol) 2,6-dibromopyridine, 1.64 g (20.0 mmol) NaOAc and 5.0 mg (0.02 mmol) $Pd(OAc)_2$ in 10 ml DMA was charged with 3.72 g (20 mmol) Ph_2PH and heated at 130°C for 12 h. The reaction mixture was poured into 100 ml of water and the precipitate formed was collected by filtration. After recrystallization from EtOH/$CHCl_3$, **18** was obtained as a colourless powder. Yield: 3.0 g (67%).

18. Found: C, 79.01; H, 5.18; P, 13.07. $C_{29}H_{23}NP_2$ (447.5). Calc.: C, 77.84; H, 5.18; P, 13.84%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 164.3 (q, $N \cong 10.4$ Hz, C1/5 (Py)); 136.4 (q, $N \cong 11.0$ Hz, C7); 135.0 (t, $J \cong 4.1$ Hz, C3 (Py)); 134.1 (t, $N \cong 20.0$ Hz, C8); 128.7 (s, C10); 128.3 (t, $N \cong 7.5$ Hz, C9); 126.5 (d, $N \cong 22.3$ Hz, C2/4 (Py)); $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −3.8 (s).

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