Water-Soluble Phosphanes, 10[◇]

Novel Syntheses of Mono- and Bisphosphonated Aromatic Phosphanes by Consecutive Pd-Catalyzed P–C Coupling Reactions and Nucleophilic Phosphanylation – X-ray Structure of $Ph_2P–C_6H_4–m\text{-}PO_3Na_2 \cdot 5.5\ H_2O \cdot$ *i*PrOH

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The triphenylphosphane derivatives **2a** and **5**, bearing one and two phosphonic ester groups, are accessible in high yields by consecutive Pd-catalyzed P–C coupling reactions of *p*-bromoiodobenzene with Ph_2PH and $PhPH_2$, respectively, and then with diethyl phosphite. Ester hydrolysis yields the highly water-soluble sodium salts of mono- and bisphosphonated triphenylphosphane, **3a** and **6**, respectively. On reaction of the *p*- and *m*-fluorophenylphosphonic diethyl esters **7a**, **7b** with Ph_2PK and subsequent ester hydrolysis the isomeric disodium (diphenylphosphano)phenylphosphonates **3a**, **3b** were obtained. The X-ray structure of $Ph_2P(C_6H_4\text{–}m\text{-}PO_3Na_2) \cdot 5.5\ H_2O \cdot$ *i*PrOH (space group $Cmc2_1$) has been determined. In the solid state, it forms a layer structure with hydrophilic (PO_3^{2-}, H_2O, *i*PrOH) and hydrophobic (Ph_2P) compartments, in which the PO_3^{2-} anionic groups are not engaged in coordination of the sodium cations.

The introduction of the aqueous two-phase technique may be considered as a cornerstone in the development of homogeneous catalysis over the last two decades. The environmental benefits of using water instead of organic solvents and the ease with which the water soluble catalyst may be separated from the products are the principal advantages of this technique. Water solubility of the complex catalysts is achieved by incorporation of phosphanes bearing cationic[2], anionic[3], or non-charged hydrophilic[4] groups, respectively. The phosphonate group has been employed only very recently as a polar functionality to enhance the solubility of aliphatic and aromatic phosphanes in aqueous media. Thus, DuBois et al.[5] have reported the syntheses of tridentate phosphane ligands bearing $(EtO)_2(O)PCH_2CH_2$ side chains. Köckritz et al.[6] and Schull, Fettinger, and Knight[7] have developed a multistep synthesis for the sodium salts of monophosphonated triphenylphosphane, moderate yields being achieved in both cases. Phosphanorbornadiene monophosphonates are formed by addition of (phenylethynyl)phosphonates to 1-phenyl-3,4-dimethylphosphole[8].

The great potential of phosphonated and phosphinated derivatives of triphenylphosphane as catalyst ligands in two-phase catalysis has been demonstrated by the Pd-catalyzed carbonylation of benzyl chloride[7] and by Suzuki-type C−C coupling reactions[9].

Syntheses of Mono- and Bisphosphonated Aromatic Phosphanes Using Consecutive Pd-Catalyzed P−C Coupling Reactions

Previously, we reported a novel synthetic route to multifunctional phosphanes by cross-coupling of aryl halides with primary or secondary phosphanes in the presence of a base and catalytic amounts of a palladium catalyst[10]. Using this method, *p*-bromophenyldiphenylphosphane[11] (**1a**) and bis(*p*-bromophenyl)phenylphosphane[12] (**4**) were obtained in high yields by reaction of *p*-bromoiodobenzene with diphenylphosphane and phenylphosphane, respectively in the presence of 0.1 mol-% $Pd(Ph_3P)_4$ (Eq. 1a, 2a). The *m* and *o* isomers **1b** and **1c** are also accessible by this synthetic procedure.

The final steps in the syntheses of the mixed-ligand phosphanophosphonates required the introduction of the phosphonic ester groups into **1a** and **4**. This was achieved by Pd-catalyzed P−C coupling reactions with diethyl phosphite, $HP(O)(OEt)_2$. The mono- (**2a**)[7] and bisphosphonated (**5**) *p* isomers were formed in high yields (Eq. 1b, 2b). The anionic derivatives **3a** and **6** were obtained by transesterification of **2a** and **5** using Me_3SiBr[14], followed by hydrolysis of the intermediate silyl esters and subsequent neutrali-

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[◇] Part 9: Ref.[1].

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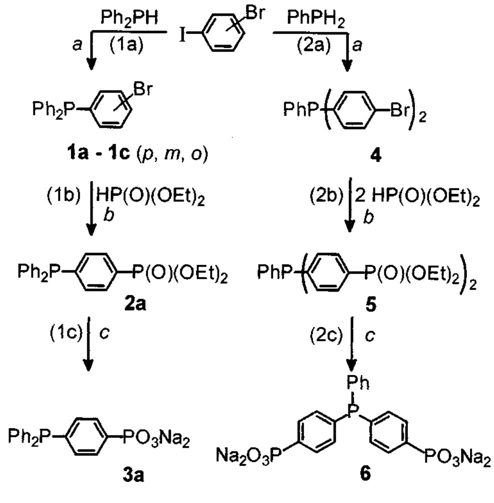
Scheme 1

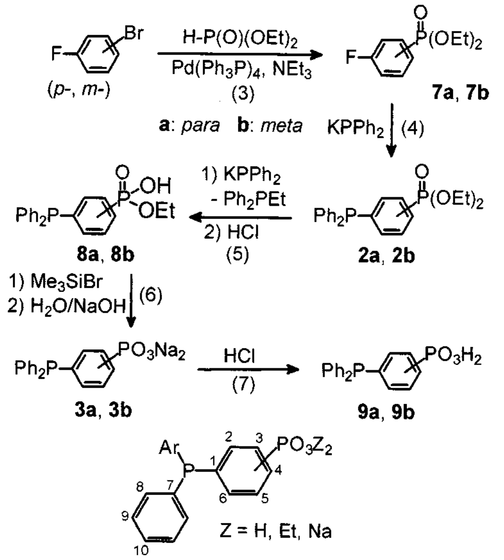


a: catalyst: $Pd(Ph_3P)_4$, $Pd(OAc)_2$; base: NEt_3, KOAc

b: catalyst: $Pd(Ph_3P)_4$; base: NEt_3

c: Me_3SiBr; H_2O/NaOH

Scheme 2



zation of the phosphonic acids with aqueous NaOH (Eq. 1c, 2c). As expected, the solubility of **6**, bearing two polar groups, was much higher (1000−1100 g/kg water, 20°C) than that of **3a** (300−400 g/kg water, 20°C).

Syntheses of *m*- and *p*-Phosphonated Aromatic Phosphanes by a Combination of Pd-Catalyzed P−C Coupling and Nucleophilic Substitution

Nucleophilic phosphanylation of fluorobenzene derivatives bearing electron-withdrawing substituents[1][3b][15] may be employed for the synthesis of a great variety of water-soluble phosphanes. In combination with the Pd-catalyzed coupling[10], the reaction has many attractive features as a general P−C bond-formation method. This is illustrated by the syntheses of the *p* and *m* isomers **2a**, **2b** of monophosphonated triphenylphosphane (Eq. 4). The starting materials, **7a**[16a], **7b**[16b], were obtained by P−C coupling reactions of *p*- and *m*-bromofluorobenzene with diethyl phosphite using catalytic amounts of $Pd(Ph_3P)_4$ in the presence of NEt_3 as the base (Eq. 3). This method was found to be more efficient than the multistep syntheses reported in the literature for **7a**[16a] and **7b**[16b].

Upon treatment of **7a** with Ph_2PK, a mixture of the expected diester **2a** and the potassium salt of the monoester **8a** was formed (Eq. 4, 5). The diester **2a** is formed initially until about half an equivalent of Ph_2PK has been added. The addition of further Ph_2PK yields Ph_2PEt and the potassium salt of **8a** as a result of dealkylation of the ester group in **2a** or **7a**. This indicates that in the initial stages of the reaction nucleophilic phosphanylation is faster than dealkylation. In contrast to our results, from a similar reaction of the *p* isomer **7a**, using Ph_2PLi instead of Ph_2PK, Köckritz et al.[6] obtained only the diester **2a** and, surprisingly, no dealkylation products were detected. However, the diester **2a** was formed only in moderate yields and no experimental details were given. Phosphanylation of diethyl *m*-fluorophenylphosphonate (**7b**) with Ph_2PK in THF solution proceeded much more slowly than that of the corresponding *p* isomer **7a**, the anion of **8b** being formed exclusively.

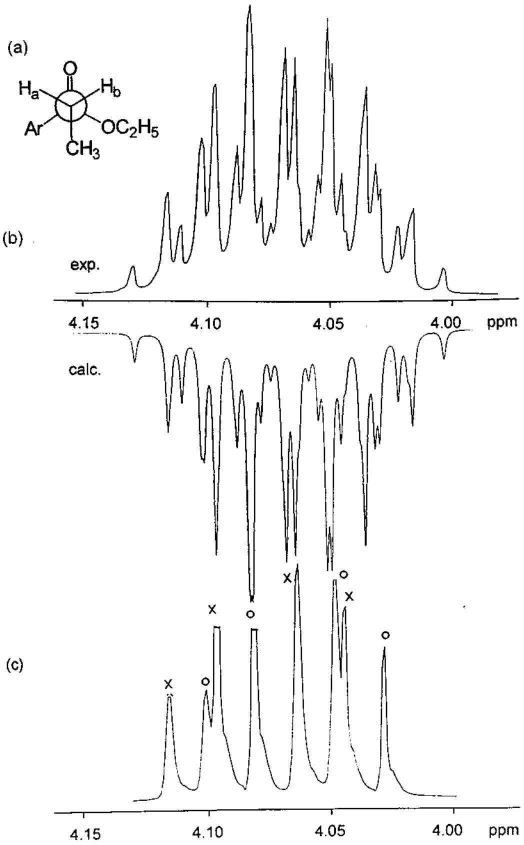
After acidification of the reaction mixtures, the monoesters **8a**, **8b** were precipitated as colorless crystals (Eq. 4, 5). Transesterification of **8a**, **8b** with Me_3SiBr and subsequent reaction of the intermediate silyl esters with NaOH gave the disodium salts **3a** and **3b**, respectively (Eq. 6), in overall yields much higher than those reported previously in the literature[7]. The free phosphonic acids **9a**, **9b** were precipitated from aqueous solutions of **3a**, **3b** on acidification with HCl (Eq. 7).

NMR-Spectroscopic Identification of 1a−11b

The $\delta P(P^{III})$ values of the phosphonated phosphanes differ only marginally from that of Ph_3P[11][17a] ($\delta P = -5.9$ to -8.0), with $\delta P(P^V)$ values (20.0−8.9) falling in the range typical for aromatic phosphonic acids and their esters[17b]. Assignment of all $^{13}C\{^1H\}$-NMR signals of **1a**−**1c**, **2a**, **3a**, **3b**, **4**, **5**, **6** and **7a**, **7b**, **9a**, **9b** was achieved with the aid of DEPT experiments[18a] and by comparison of the δC values and P−C coupling constants with the relevant data for Ph_3P[18b]. Further support was gained from the relative magnitude of the coupling constants $^nJ(PC)$, which decrease in the order $^2J(PC) > {}^3J(PC) > {}^4J(PC)$, with $^1J(PC)$ being smaller than $^2J(PC)$[18c]. Large coupling constants (160−190 Hz) are observed for the signals of the carbon atoms (C3 or C4, respectively) bound to P^V[18d] (for the numbering of the carbon atoms in the Experimental Section see Scheme 2).

The protons of the CH_2 groups of the $P(O)(OEt)_2$ substituents in **2a**, **7a**, and **7b** are diastereotopic[19] (Figure 1a, **7a**). In the ^1H-NMR spectra, complicated multiplet patterns are observed, representing the AB parts of ABM_3X spin systems [A, B = $H_{a,b}(CH_2)$, M = $H(CH_3)$, X = ^{31}P]. Analysis of these line patterns (Figure 1b) could be accomplished in the case of **7a** using $^1H\{^1H(CH_3)\}$ homo nuclei decoupling experiments (Figure 1c).

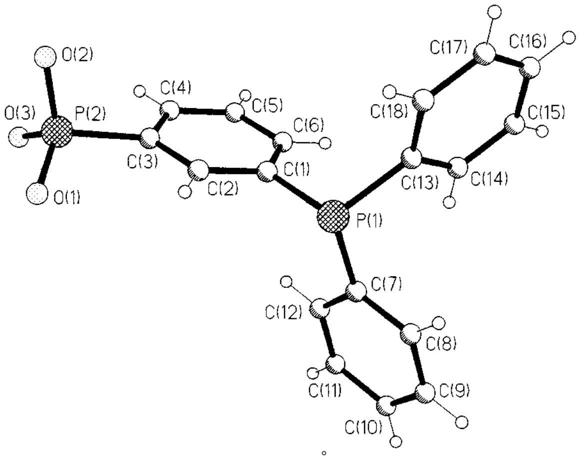
Figure 1. (a) Newman projection along the P···(O)···C(H_2) axis. − (b) ^1H-NMR spectrum of **7a** (experimental/calculated); δH_a = 4.06, δH_b = −4.12, $^2J(H_aH_b)$ = 10.2, $^3J(H_aP)$ = 8.2, $^3J(H_bP)$ = 7.8, $^3J(HH)$ = 7.1 Hz. − (c) $^1H\{^1H(CH_3)\}$-NMR spectrum of **7a**, P(O)(O−CH_2−CH_3)$_2$ group



X-ray Structure of $Ph_2P(C_6H_4-m\text{-}PO_3Na_2)\cdot$ 5.5 $H_2O\cdot i$PrOH

Colorless crystals of the composition $Ph_2P(C_6H_4-m\text{-}PO_3Na_2)\cdot 5.5\ H_2O\cdot i$PrOH were formed at the interface between the two layers obtained on addition of 2-propanol to a concentrated aqueous solution of **3b**. The results of an X-ray structural analysis are shown in Figures 2 and 3, crystallographic data are collected in Table 1, and selected bond lengths and angles are given in the caption to Figure 2. A comparison of the structural parameters of triphenylphosphane[20] with those of the isolated diphenylphosphanophenyl-*m*-phosphonate dianion of **3b** and its *p* isomer **3a**[7], reveals that the PO_3^{2-} group in the *p* or *m* position of the aromatic ring system has only marginal influence on the geometry of the triarylphosphane subunit. The propeller-like arrangement of the phenyl rings (Figure 2), which are each rotated in the same sense, is found in all three structures. In contrast to $Na_2[Ph_2P(C_6H_4-p\text{-}PO_3)(H_2O)_3(CH_3OH)](CH_3OH)$[7], which is dimeric and contains two formula units in the unit cell, the phosphorus atom in the phosphonate group of $Na_2[Ph_2P(C_6H_4-m\text{-}PO_3)\cdot 5.5\ H_2O\cdot i$PrOH] displays only a slightly distorted tetrahedral geometry. The O−P−O bond angles and P−O bond lengths are identical within experimental standard deviation, and the P−O distances fall within the typical range[21][22].

Figure 2. Structure of the anion of **3b**[a]



[a] Selected interatomic distances [Å] and angles [°]: P(1)−C(1) 1.843(5), P(1)−C(7) 1.836(8), P(1)−C(13) 1.842(8), P(2)−C(3) 1.823(5), P(2)−O(1) 1.522(6), P(2)−O(2) 1.520(7), P(2)−O(3) 1.521(7); C(1)−P(1)−C(7) 103.7(4), C(7)−P(1)−C(13) 101.9(4), C(1)−P(1)−C(13) 102.6(4), C(2)−C(1)−P(1) 116.6(4), C(6)−C(1)−P(1) 123.3(4), O(1)−P(2)−O(2) 111.9(4), O(1)−P(2)−O(3) 111.6(4), O(2)−P(2)−O(3) 110.9(4).

Within the unit cell, the sodium cations are solvated by water and 2-propanol, thus forming a three-dimensional network supported by O···H−O hydrogen bonding (Figure 3). The shortest distance between the oxygen atoms of the $Ph_2P(C_6H_4-m\text{-}PO_3^{2-})$ dianions and the sodium atoms is 2.987(6) Å [O(1)−Na(1)]. This is around 0.45−0.60 Å larger than that of other Na−O interactions in the structure, implying that the phosphonate groups are not engaged in the primary coordination sphere of the sodium. The Na···O(P) distances found in $Na_2[Ph_2P(C_6H_4-p\text{-}PO_3)(H_2O)_3(CH_3OH)](CH_3OH)$[7] [Na(1)−O(2) 2.448(3), Na(2)−O(1) 2.249(3) Å] are shorter than the closest Na−O contact in $Na_2[Ph_2P(C_6H_4-m\text{-}PO_3)\cdot 5.5\ H_2O\cdot i$PrOH] [Na(1)−O(1) 2.987(6) Å]. Interestingly, the structure contains sodium cations in three different environments. Na(1) is coordinated to five water molecules in a trigonal-bipyramidal arrangement (Na···O distances 2.30−2.58 Å), two of the water molecules [O(13), O(14)] form bridges to the hexacoordinate Na(2) (Na···O distances 2.36−2.46 Å), which in turn is connected to Na(3) and symmetry-equivalent Na(3a) via two water molecules [O(21a), O(21)] in axial positions. Na(3a) is pentacoordinated, with the two axial positions in a strongly distorted trigonal-bipyramid being occupied by bridging oxygen atoms [O(21a) and O(12c)]. 2-Propanol and two water oxygen atoms lie in the equatorial plane of Na(3), with one of the latter [O(22)] bridging the symmetry-related Na cations [Na(3) and Na(3a)]. The closest cation−cation contact is 3.314(6) Å [Na(2)···Na(3)].

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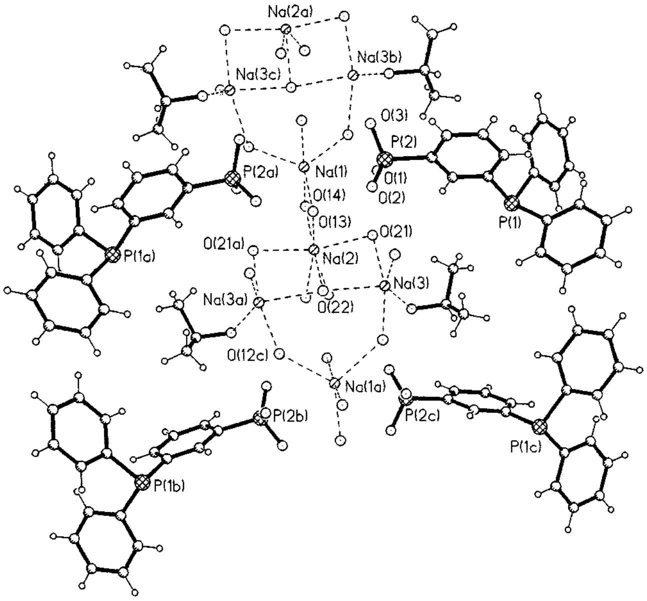
Figure 3. Solid-state structure of **3b**·5.5 H_2O·*i*PrOH



Experimental Section

For experimental details see Part 9 of this series[1]. Phenylphosphane, diphenylphosphane[23], and $Pd(Ph_3P)_4$[13] were prepared according to literature methods. Ph_2PK, 2-, 3-, and 4-bromoiodobenzene, 3- and 4-bromofluorobenzene, as well as bromotrimethylsilane were purchased from Aldrich Chemical Co. and used without further purification.

Preparation of **1a−1c** *by Palladium-Catalyzed Coupling of 2-, 3-, and 4-Bromoiodobenzene with Ph_2PH:* A mixture of 20.0 g (70.8 mmol) of the appropriate bromoiodobenzene, 7.64 g (78.0 mmol) of potassium acetate, and 28.4 ml of a $5.0 \cdot 10^{-3}$ M solution of palladium(II) acetate in dimethylacetamide was dissolved in 120 ml of dimethylacetamide. To this solution, 13.16 g (70.8 mmol) Ph_2PH was added and the mixture was heated for 5 d at 130°C. The reaction mixture was then poured into 200 ml of deoxygenated water and the resulting suspension was extracted with 200 ml of dichloromethane. The organic phase was separated, washed with 100 ml of saturated aqueous KCl solution, and dried with magnesium sulfate. After removal of the solvent under reduced pressure (20°C, 10 mbar), the residue was distilled in vacuo (0.1 mbar) at 200−300°C. Yields: 15.0 g (62%) **1a**, 18.4 g (76%) **1b**, 18.0 g (75%) **1c**. For further purification, **1a−1c** were recrystallized from water/ethanol.

1a: $C_{18}H_{14}BrP$ (341.2): calcd. C 63.36, H 4.14; found C 63.32, H 4.18. − MS: $[M^+]$: *m/z* = 342 (^{81}Br), 340 (^{79}Br). − $^{31}P\{^1H\}$ NMR (C_6D_6): δP = −4.8. − $^{13}C\{^1H\}$ NMR (C_6D_6): δC (C1−C10) = 137.0 (14.2), 135.4 (20.3), 131.8 (7.1), 123.5, 131.8 (7.1), 135.4 (20.3), 137.2 (12.2), 133.9 (19.3), 128.7 (7.1), 128.9. − **1b**: $C_{18}H_{14}BrP$ (341.2): calcd. C 63.36, H 4.14; found C 63.40, H 4.21. − MS: $[M^+]$: *m/z* = 342 (^{81}Br), 340 (^{79}Br). − $^{31}P\{^1H\}$ NMR (C_6D_6): δP = −3.3. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δC (C1−C10) = 141.4 (16.3), 136.4 (20.3), 123.6 (7.1), 132.1, 123.6 (7.1), 136.4 (19.3), 136.8 (12.2), 134.2 (19.3), 129.1 (7.1), 129.5. − **1c**: $C_{18}H_{14}BrP$ (341.2): calcd. C 63.36, H 4.14; found C 63.30, H 4.22. − MS: $[M^+]$: *m/z* = 342 (^{81}Br), 340 (^{79}Br). − $^{31}P\{^1H\}$ NMR (C_6D_6): δP = −3.3. − $^{13}C\{^1H\}$ NMR (C_6D_6): δC (C1−C10) = 139.7 (13.2), 130.5 (30.0), 133.2 (2.0), 130.1, 127.4, 134.7, 136.6 (12.2), 134.3 (21.4), 128.8 (7.1), 129.0.

Preparation of **4** *by Pd-Catalyzed Coupling of 4-Bromoiodobenzene with $PhPH_2$:* A Schlenk flask was charged with 250 ml of acetonitrile, 7.91 g (71.8 mmol) of phenylphosphane, 40.65 g (143.7 mmol) of 4-bromoiodobenzene, and 16.00 g (158.1 mmol) of triethylamine. The mixture was deoxygenated and 1.66 g (1.43 mmol, 1 mol-%) of $Pd(Ph_3P)_4$ was added. After heating the reaction mixture under reflux for 24 h, the solvent was removed in vacuo, and the residue was dissolved in 200 ml of dichloromethane. The resulting solution was washed with three 100-ml aliquots of water. The organic phase was separated and dried with magnesium sulfate. After removal of the solvent under reduced pressure (30°C, 10 mbar), the residue was distilled in vacuo (0.1 mbar) at 200−300°C. Yield: 19.03 g (63%). − **4**: $C_{18}H_{13}Br_2P$ (420.1): calcd. C 51.47, H 3.12; found C 51.12, H 3.25. − MS: $[M^+]$: *m/z* = 418 (^{79}Br), 420 ($^{81}Br,^{79}Br$), 422 (^{81}Br). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δP = −6.0; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δC (C1−C10) = 135.9 (12.2), 135.1 (20.3), 131.7 (7.1), 123.6, 131.7 (7.1), 135.1 (20.3), 136.0 (10.2), 133.6 (19.3), 128.7 (7.1), 129.2.

Preparation of **2a/3a** *and* **5/6**: To a solution of 2.0 g (5.9 mmol) of **1a** or 4.26 g (10.1 mmol) of **4** in 40 or 80 ml of toluene, 0.89 g (6.45 mmol) or 3.08 g (22.3 mmol) of $HP(O)(OEt)_2$ and 0.65 g (6.45 mmol) or 2.26 g (22.3 mmol) of NEt_3 were added. After deoxygenation in vacuo, 68 mg (0.06 mmol, 1 mol-%) or 0.23 g (0.2 mmol, 1 mol-%) of $Pd(Ph_3P)_4$ was added. The reaction mixtures were then heated to 80°C for 50 h or 72 h. After cooling to ambient temperature and washing with three 25- or 50-ml aliquots of water, the toluene phases were collected and dried with $MgSO_4$. Evaporation of the solvent in vacuo left **2a** and **5** as yellow, viscous oils. Yields: 1.46 g (62%) **2a**, 3.78 g (70%) **5**. − **2a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δP = −3.8 (P^{III}), 19.4 (P^V). − **5**: MS: $[M^+]$: *m/z* = 534. − $^{31}P\{^1H\}$NMR ($CDCl_3$): δP = −3.4 (P^{III}), 19.3 (P^V).

To a solution of 3.79 g (7.1 mmol) of **5** in 50 ml of dichloromethane at room temperature 6.5 g (42.4 mmol) of Me_3SiBr were added with stirring. After 12 h, all volatiles were removed in vacuo (60°C, 0.01 mbar) and the residual oily liquid was taken up in 50 ml of acetone. To the resulting solution 1.02 g (56.7 mmol) of water was added and the mixture was stirred at ambient temperature for 2 h. Thereafter, all volatiles were removed in vacuo (20°C, 0.01 mbar), and the pale-yellow solid (the free phosphonic acid) thus obtained was redissolved in 20 ml of conc. NaOH solution. On pouring this solution into 200 ml of ethanol, **6** was precipitated as pale-yellow crystals, which were separated by suction using a fritted Buchner funnel. The residue was washed with two 10-ml aliquots of ethanol and dried in vacuo (60°C, 0.01 mbar). Yield: 2.58 g (71.2%) **6**.

3a was obtained in high yield by the analogous procedure using **2a** as the starting material.

3a: $^{31}P\{^1H\}$ NMR (D_2O): δP = −5.5 (P^{III}), 12.0 (P^V). − **6**: $C_{18}H_{13}O_6Na_4P_3 \cdot 1.5\ H_2O$ (537.2): calcd. C 40.25, H 3.00; found C 40.19, H 3.24. − $^{31}P\{^1H\}$ NMR (D_2O): δP = −6.0 (P^{III}), 12.0 (P^V). − $^{13}C\{^1H\}$-NMR (D_2O): δC (C1−C10) = 138.5 (5.1, 3.1), 135.1 (18.8, 13.2), 132.8 (8.1, 8.1), 144.3 (165.8), 132.8 (8.1, 8.1), 135.1 (18.8, 13.2), 138.3 (5.1), 136.0 (19.3),131.2 (7.1), 131.7.

Preparation of **7a**, **7b**: A Schlenk flask was charged with 200 ml of toluene, 20.0 g (114.3 mmol) of 4-bromofluorobenzene or 25.0 g (142.8 mmol) of 3-bromofluorobenzene, 17.3 g (125.7 mmol) or 21.7 g (157.1 mmol) of $HP(O)(OEt)_2$, and 12.7 g (125.7 mmol) or 15.9 g (157.1 mmol) of NEt_3. Dissolved oxygen was removed by freeze-thaw cycles and after addition of 5.3 g (4.6 mmol, 4 mol-%) or 6.6 g (5.7 mmol, 4 mol-%) of $Pd(Ph_3P)_4$ the reaction mixture was heated to 70−80°C for 24 h. Thereafter, the mixture was washed with three 200-ml aliquots of water. The toluene phase was dried with $MgSO_4$. The liquid obtained after removal of the solvent in vacuo was fractionated. Yields: 21.5 g (81%) **7a**, 28.0 g (84%) **7b**.

7a: $C_{10}H_{14}FO_3P$ (232.2): calcd. C 51.73, H 6.08, P 13.34; found C 51.94, H 6.18, P 13.13. − B.p. 96°C, 0.4 mbar. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P = 18.9$ [$^5J(PF) = 1.4$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δC (C1−C6) = 165.4 [4.1, 253.8 $^1J(CF)$], 115.8 (16.3, 21.4), 134.4 (11.2, 8.6), 124.7 (192.8, 3.6), 134.4 (11.2, 8.6), 115.8 (16.3, 21.4), 62.2 (5.6, CH_2), 16.3 (6.6, CH_3). − **7b**: $C_{10}H_{14}FO_3P$ (232.2): calcd. C 51.73, H 6.08; found C 51.64, H 6.13. − B.p. 96°C, 0.4 mbar. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P = 17.4$ [$^4J(PF) = 8.6$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δC (C1−C6) = 162.3 (21.2, 249.2), 118.3 (10.2, 22.4), 131.2 (188.2, 6.1), 127.3 (9.2, 3.1), 130.4 (17.3, 8.1), 119.3 (3.1, 21.4), 62.2 (6.1, CH_2), 16.1 (6.1, CH_3).

Nucleophilic Phosphination of **7a** *with* Ph_2PK *in a 1:1 Molar Ratio:* To the solution of 1.63 g (7.0 mmol) **7a** in 20 ml of THF 17 ml of a 0.5 M solution of Ph_2PK in THF (8.5 mmol) was added at room temp. After completion of the addition, the solvent was evaporated under reduced pressure. From the oily residue Ph_2PEt formed during the reaction was removed at 100°C, 0.01 mbar using a short-path distillation apparatus. The remaining solid was extracted with a mixture of 20 ml of water and CH_2Cl_2. The organic phase was separated and dried with magnesium sulfate. After removal of the solvent in vacuo, **2a** was obtained as a colorless oil. Yield: 1.52 g (54.5%).

2a: $C_{22}H_{24}O_3P_2$ (398.4): calcd. C 66.33, H 6.07, P 15.55; found C 65.49, H 6.29 P 14.60. − MS: [M^+]: *m/z* = 398. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P = -3.8$ (P^{III}), 19.4 (P^V). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δC (C1−C10) = 143.6 (15.3, 3.1), 133.2 (18.3, 14.2), 131.6 (6.1, 12.2), 128.7 (188.2), 131.6 (6.1, 12.2), 133.2 (18.3, 14.2), 136.2 (10.2), 134.0 (20.3), 128.8 (7.1), 129.3, 62.2 (5.1, CH_2), 16.5 (6.1, CH_3).

Synthesis of **8a** *and* **8b**: A 0.5 M solution of Ph_2PK (250 mmol) in 500 ml of THF was added to 27.86 g (120 mmol) of **7a** dissolved in 500 ml of THF over a period of 3 h at 20°C. After completion of the addition, the reaction mixture was stirred for a further 1 h. Thereafter, the solvent was distilled off under normal pressure and the remaining residue was partitioned between 500 ml of water and 500 ml of dichloromethane. The organic phase was separated and dried with magnesium sulfate. The residue obtained after evaporation of the solvent at normal pressure was fractionated in vacuo (0.1 mbar) to afford 11.10 g of Ph_2PEt (b.p. 102°C, 0.1 mbar, yield 43%). The aforementioned aqueous phase was treated with HCl until a pH value of 2 was reached, and then extracted with three 150-ml aliquots of dichloromethane. The combined extracts were dried with magnesium sulfate. Removal of the solvent in vacuo left a colorless solid. Yield: 36.50 g (82%) **8a**.

8b was obtained in an analogous manner starting from 6.82 g (29.4 mmol) of **7b**, dissolved in 100 ml of THF, and 130 ml of a 0.5 M solution of Ph_2PK (65.0 mmol) in THF. Due to the lower reactivity of **7b**, a longer reaction time was needed, even at reflux temperature (72 h). Yield: 8.80 g (81%).

8a: $C_{20}H_{20}O_3P_2$ (370.3): calcd. C 64.87, H 5.44, P 16.73; found C 64.72, H 5.38, P 16.56. − MS: [M^+]: *m/z* = 370. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P = -3.6$ (P^{III}), 20.0 (P^V). − **8b**: $C_{20}H_{20}O_3P_2$ (370.3): calcd. C 64.87, H 5.44, P 16.73; found C 64.19, H 5.32, P 16.14. − MS: [M^+]: *m/z* = 370. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P = -3.9$ (P^{III}), 19.9 (P^V).

Preparation of **3a** *and* **3b**: To the solutions of 35.54 g (96.0 mmol) of **8a** or 8.11 g (21.9 mmol) of **8b** in 300 ml or 100 ml of dichloromethane 44.08 g (287.9 mmol) or 10.1 g (66.0 mmol) of Me_3SiBr was added. After stirring the reaction mixtures for 12 h at ambient temperature, all volatiles were removed in vacuo (60°C, 0.01 mbar). The intermediate silyl esters formed were obtained as very moisture-sensitive colorless oils. They were dissolved in acetone (300 ml or 100 ml, respectively), 4.13 g (229.4 mmol) or 1.44 g (80.0 mmol) of water was added and the reaction mixture was stirred at ambient temperature for 2 h. After removal of all volatiles in vacuo (20°C, 0.01 mbar), the respective diphenylphosphanophenylphosphonic acid was obtained as a colorless solid. The product was redissolved in 150 ml or 50 ml of conc. NaOH and the resulting solution was poured into 4.0 l or 400 ml of ethanol, whereupon the disodium salt of the diphenylphosphanophenylphosphonic acid was precipitated as colorless crystals. The product was filtered off using a Buchner funnel, washed with ethanol, and dried in vacuo (60°C, 0.01 mbar). Yields: 30.5 g (76%) **3a**, 5.81 g (63%) **3b**.

3a: $C_{18}H_{14}Na_2O_3P_2 \cdot 2\ H_2O$ (422.2): calcd. C 51.20, H 4.30; found C 51.43, H 4.34. − $^{31}P\{^1H\}$ NMR (D_2O): $\delta P = -5.5$ (P^{III}), 12.0 (P^V). − $^{13}C\{^1H\}$ NMR (D_2O): δC (C1−C10) = 136.8 (9.2, 2.0), 132.9 (19.3, 13.2), 130.7 (7.1, 8.1), 142.2 (166.8), 130.7 (7.1, 8.1), 132.9 (19.3, 13.2), 136.2 (6.1), 133.8 (19.3), 129.0 (7.1), 129.4. − **3b**: $C_{18}H_{14}Na_2O_3P_2 \cdot 2\ H_2O$ (422.2): calcd. C 51.20, H 4.30; found C 51.34, H 4.39. − $^{31}P\{^1H\}$ NMR (D_2O): $\delta P = -5.1$ (P^{III}), 11.8 (P^V). − $^{13}C\{^1H\}$ NMR (D_2O): δC (C1−C10) = 135.3 (12.2, 7.1), 136.1 (29.6, 9.5), 141.8 (9.2, 165.8), 133.2 (9.2), 128.4 (4.1, 12.2), 131.5 (9.2), 136.3 (6.1), 133.7 (18.3), 129.0 (8.1), 129.3.

The diphenylphosphanophenylphosphonic acids **9a** and **9b** were obtained as oily liquids in quantitative yields by acidification of aqueous solutions of the disodium salts **3a** and **3b** with HCl. The crude products were extracted with dichloromethane, and the combined extracts were dried with magnesium sulfate. After evaporation of the solvent, the diphenylphosphanophenylphosphonic acids **9a** and **9b** were obtained as colorless solids. The products were characterized by $^{31}P\{^1H\}$-NMR spectroscopy and APCI mass spectrometry. **9a**, **9b**: APCI-MS: [MH^+]: *m/z* = 343; [$MH^+ - PO_2H$]: *m/z* = 279; [$MH^+ - PO_3H$]: *m/z* = 263.

Crystal-Structure Analysis of $Na_2[Ph_2P(C_6H_4{-}m{-}PO_3) \cdot 5.5\ H_2O \cdot iPrOH]$*:* Experimental data for the X-ray structural analysis are collected in Table 1. Unit-cell constants were determined from a least-squares fit to the settings of 25 reflections centred on a Siemens P4 diffractometer. Intensity data were collected with the

Table 1. Experimental data for the X-ray structure of **3b**·5.5 H_2O·*i*PrOH

formula weight	533.30
temperature	293(2) K
crystal system	orthorhombic
space group	$Cmc2_1$
unit cell dimensions	$a = 48.462(10)$ Å
	$b = 6.3360(10)$ Å
	$c = 17.509(4)$ Å
	$\alpha = \beta = \gamma = 90°$
V	5376(2) Å^3
Z	8
$D_{calcd.}$	1.318 Mg/m^3
absorption coefficient	0.240 mm^{-1}
$F(000)$	2200
crystal size	0.46 × 0.4 × 0.06 mm
θ range	2.33 to 25.01
reflections collected	2482
independent reflections	2482
absorption correction	semiempirical
max. and min. transmission	0.589 and 0.536
data/restraints/parameters	2479/1/291
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0694$, $wR2 = 0.1339$
R indices all data	$R1 = 0.1408$, $wR2 = 0.1691$
largest diff. peak and hole	0.382/−0.315 eÅ^{-3}

diffractometer in the ω-mode (Mo-K_α radiation) and were corrected for absorptions on the basis of ψ-scan information for selected reflections. The structure was solved by direct methods (SHELXS) and refined against F^2 by full-matrix least squares (SHELXL) to $R = 0.069$ [for $I > 2\sigma(I)$] and $wR2 = 0.169$ for all independent reflections. Non-hydrogen atoms were refined anisotropically. H atoms of *i*PrOH were included at geometrical positions using the riding model (C−H = 0.96 A)[24].

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[1] M. Hingst, M. Tepper, O. Stelzer, *Eur. J. Inorg. Chem.* **1998**, 73.

[2] R. T. Smith, R. K. Ungar, L. J. Sanderson, M. C. Baird, *Organometallics* **1983**, *2*, 1138; F. Bitterer, S. Kucken, O. Stelzer, *Chem. Ber.* **1995**, *128*, 275; A. Heßler, O. Stelzer, H. Dibowski, K. Worm, F. P. Schmidtchen, *J. Org. Chem.* **1997**, *62*, 2362; H. Dibowski, F. P. Schmidtchen, *Tetrahedron* **1995**, *51*, 2325.

[3] [3a] E. Kuntz, *Chemtech.* **1987**, 570; E. Kuntz, *Fr. Pat.* 2.314.910, **1975** (Rhone-Poulenc Recherche). − [3b] F. Bitterer, O. Herd, A. Heßler, M. Kühnel, K. Rettig, O. Stelzer, W. S. Sheldrick, S. Nagel, N. Rösch, *Inorg. Chem.* **1996**, *35*, 4103; O. Herd, A. Heßler, K. P. Langhans, O. Stelzer, W. S. Sheldrick, N. Weferling, *J. Organomet. Chem.* **1994**, *475*, 99. − [3c] W. Keim, R. P. Schulz, *J. Mol. Catal.* **1994**, *92*, 21; V. Ravindar, H. Hemling, H. Schumann, J. Blum, *Synth. Commun.* **1992**, *22*, 841.

[4] D. E. Bergbreiter, L Zhang, V. Mariagnanam, *J. Am. Chem. Soc.* **1993**, *115*, 9295; M. Beller, J. G. E. Krauter, A. Zapf, *Angew. Chem.* **1997**, *109*, 793; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 793.

[5] A. Miedaner, C. J. Curtis, R. M. Barkley, D. L. DuBois, *Inorg. Chem.* **1994**, *33*, 5482.

[6] A. Köckritz, A. Weigt, M. Kant, *Phosphorus Sulfur Silicon* **1996**, *117*, 287.

[7] T. L. Schull, J. C. Fettinger, D. A. Knight, *Inorg. Chem.* **1996**, *35*, 6717.

[8] S. Lelievre, F. Mercier, F. Mathey, *J. Org. Chem.* **1996**, *61*, 3531.

[9] S. Haber, H. J. Kleiner, WO 97/05104 (Hoechst AG), 13. 2. **1997**.

[10] O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem.* **1996**, *522*, 69.

[11] L. Maier in *Organic Phosphorus Compounds*, vol. 1 (Eds.: G. M. Kosolapoff, L. Maier), Wiley-Interscience, New York, London, Sydney, Toronto, **1972**, p. 1.

[12] M. Kumada, K. Noda, *Mem. Fac. Eng. Osakke City Univ.* **1962**, *4*, 173; *Chem. Abstr.* **1963**, *59*, 8782.

[13] C. A. Tolman, W. C. Seidel, D. H. Gerlach, *J. Am. Chem. Soc.* **1972**, *94*, 2669; D. R. Coulson, *Inorg. Synth.* **1972**, *13*, 121.

[14] C. E. McKenna, J. Schmidhauser, *J. Chem. Soc., Chem. Commun.* **1979**, 739; C. J. Salomon, E. Breuer, *Tetrahedron Lett.* **1995**, *36*, 6759.

[15] M. Tepper, O. Stelzer, T. Häusler, W. S. Sheldrick, *Tetrahedron Lett.* **1997**, *38*, 2257.

[16] [16a] H. Schindlbauer, *Chem. Ber.* **1967**, *100*, 3432. − [16b] R. C. Grabiak, J. A. Miles, G. M. Schwenzer, *Phosphorus Sulfur* **1980**, *9*, 197; H. Schindlbauer, W. Prikoszovich, *Chem. Ber.* **1969**, *102*, 2914.

[17] [17a] S. Berger, S. Braun, H. O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, vol. 3 ("^{31}P-NMR Spektroskopie"), Georg Thieme Verlag, Stuttgart, New York, **1993**, p. 4. − [17b] K. Worms, M. Schmidt-Dunker in *Organic Phosphorus Compounds*, vol. 7 (Eds.: G. M. Kosolapoff, L. Maier), Wiley-Interscience, New York, London, Sydney, Toronto, **1976**, p. 6.

[18] [18a] D. P. Burum, R. R. Ernst, *J. Magn. Reson.* **1980**, *39*, 163; M. R. Bendall, D. M. Doddrell, D. T. Pegg, *J. Am. Chem. Soc.* **1981**, *103*, 4603. − [18b] H. O. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR Spectroscopy, Georg Thieme Verlag, Stuttgart, New York, **1984**, p. 424. − [18c] L. D. Quin in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade, L. D. Quin), VCH Publishers, Deerfield Beach, FL, **1987**, p. 391. − [18d] G. A. Gray, *J. Am. Chem. Soc.* **1971**, *93*, 2132.

[19] T. H. Siddall, W. E. Stewart in *Progress in Nuclear Magnetic Resonance Spectroscopy*, vol. 5 (Eds.: J. W. Emsley, J. Feeney, L. H. Sutcliffe), Pergamon Press, Ltd., Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunschweig, **1969**, p.33.

[20] B. J. Dunne, A. G. Orpen, *Acta Crystallogr.* **1991**, *C47*, 345.

[21] G. Cao, V. M. Lynch, J. S. Swinnea, T. E. Mallouk, *Inorg. Chem.* **1990**, *29*, 2112.

[22] C. Bhardwaj, H. Hu, A. Clearfield, *Inorg. Chem.* **1993**, *32,* 4294.

[23] M. Baudler, A. Zarkadas, *Chem. Ber.* **1971**, *104*, 3519; G. U. Spiegel, O. Stelzer, *Chem. Ber.* 1990, *123*, 989; W. Gee, R. A. Shaw, B. C. Smith, *Inorg. Synth.* **1967**, *9*, 19.

[24] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD 407786.

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