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Hydrophosphanation of Phenolic Aldehydes as Facile Synthetic Approach to Catechol-Functionalized Phosphane Oxides and Phosphanes

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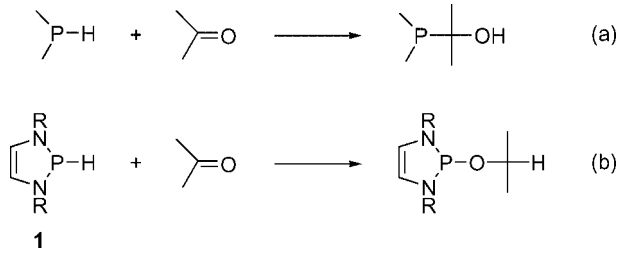
Reactions of diphenylphosphane with mono- and dihydroxybenzaldehydes yield as initial products α-phosphanyl-carbinols that exist according to NMR studies in dynamic equilibrium with the starting materials in solution but are stable in the solid state. The facile rearrangement of the initial products yields isomeric phosphane oxides which react with MeI and excess $LiAlH_4$ via deoxygenation to give the corresponding phosphanes. Phosphane oxides and phosphanes were isolated and characterized by analytical and spectroscopic data. The reactions described represent an improved synthesis for phosphanes with phenol and catechol functionalities that are useful for applications as ligands or supramolecular building blocks.

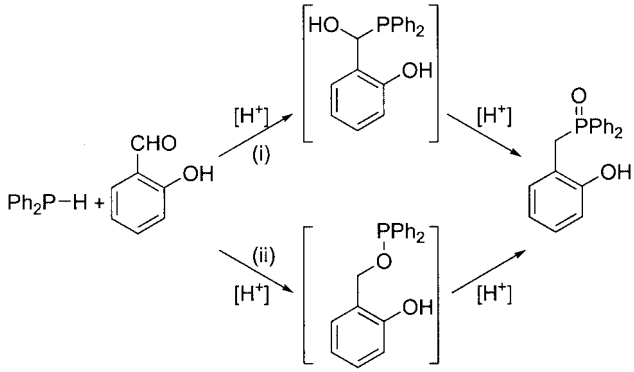
Introduction

The addition of a P–H bond to a carbonyl group is a fundamental and synthetically useful reaction of phosphorus-hydrogen substituted phosphanes PH_nR_{3-n}. These transformations proceed normally strictly regioselective via P–C bond formation to give α-phosphanyl-carbinols (Scheme 1, a) and are used for the synthesis of functional tertiary phosphanes.[1] We have recently found that N-heterocyclic phosphanes **1** react with aldehydes and ketones via reduction rather than alkylation of the carbonyl moiety (Scheme 1, b).[2] The reversed regioselectivity ("umpolung") has been related to the unique hydride-like polarization of the P–H bond in **1** which owes to the special bonding situation in the heterocycle.[2]



Scheme 1. Possible reaction modes of phosphanes with carbonyl groups.

During a study on hydrophosphanation of carbonyl compounds we noticed that the reaction of diphenylphosphane with salicylic aldehyde affords a benzylphosphane oxide. Similar reactions were observed earlier and explained by a two-step sequence involving a "normal" hydrophosphanation followed by isomerization of the transient α-phosphanyl-carbinol [pathway (i), Scheme 2].[3] In the context of our studies on controlling the regioselectivity in hydrophosphanations[2] it was of interest to elucidate mechanistic aspects of this reaction in more detail. In particular, we wanted to exclude that the product was formed via "inverse" addition of the P–H bond of the phosphane and subsequent Michaelis–Arbuzov rearrangement of a transient phosphinite [pathway (ii) in Scheme 2] which might, in view of the reactivity of **1** and earlier observations of Michaelis–Arbuzov rearrangements under conditions similar to the ones applied here,[4] provide a conceivable alternative to the standard mechanism. We present here the results of studies of the transformations of diphenylphosphane and phenolic aldehydes into phenol-functionalized phosphane oxides, and demonstrate that these species can easily be converted into phosphanes. The products thus accessible belong to a class of multifunctional ligands that have recently attracted increasing attention as supramolecular building blocks[5]



Scheme 2.

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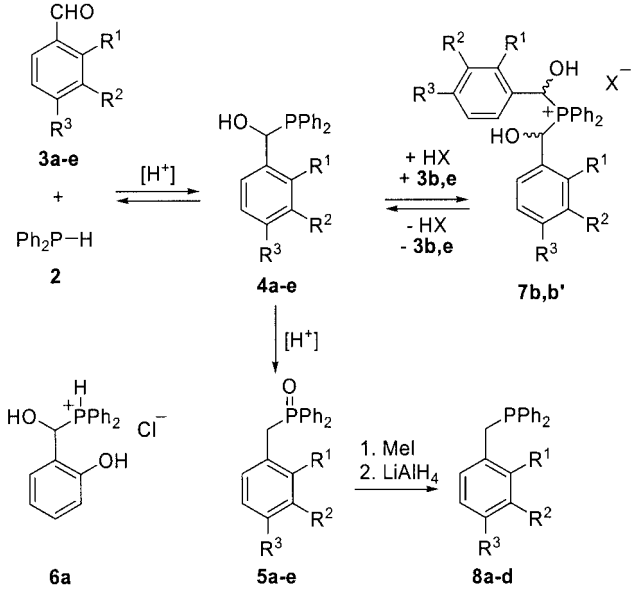
and anchoring groups that are capable of immobilizing metal complexes on the surface of a metal oxide support.[6]

Results and Discussion

The reaction of equimolar amounts of diphenylphosphane (**2**) and salicylic aldehyde (**3a**) in methanol or ethers (Et_2O, DME) in the presence of catalytic amounts of hydrochloric or *p*-toluenesulfonic acid affords directly the phosphane oxide **5a**[7] which has been isolated in good yield after work-up (Scheme 3).



	3a–9a	3b–8b	3c–8c	3d–8d	3e–7e
R^1	OH	OH	H	H	H
R^2	H	OH	H	OH	OH
R^3	H	H	OH	OH	H

X = 4-CH_3–$C_6H_4SO_3^-$

Scheme 3.

^{31}P NMR studies revealed that **5a** remained the only spectroscopically detectable species beside unreacted **2** and minor side products. The latter were not further characterized but their chemical shifts precluded assignment as an α-phosphanyl-carbinol. In order to elucidate mechanistic details we set out to find reaction conditions that facilitated the detection of a precursor to **5a**. In these studies it was established that treatment of an ethereal solution of **2** and **3a** with excess concd. hydrochloric acid lead to immediate precipitation of a colorless solid which was isolated by filtration. A solid-state ^{31}P CP/MAS NMR spectrum disclosed an isotropic shift ($\delta^{31}P_{iso}$ = –0.8) which differs clearly from that of **5a** ($\delta^{31}P_{iso}$ = 39.3) but resembles that of the α-phosphanyl-carbinol obtained from reaction of **2** and benzaldehyde. A spectrum recorded under conditions that allow to detect scalar couplings to protons revealed a doublet splitting attributable to a one-bond *J*-coupling (Figure 1, J_{PH} = 501 Hz). Consequently, we assume that α-phosphanyl-carbinol hydrochloride **6a** is formed which is deemed to represent the initial product formed by attack of the phosphane on the protonated aldehyde. This structural assignment was further corroborated by satisfactory analytical data. Attempts to characterize **6a** by solution NMR spectroscopy revealed that the product decomposes upon dissolution in methanol to give a mixture of the starting materials and the phosphane oxide **5a**, an observation that emphasizes the character of a reaction intermediate for **6a**.

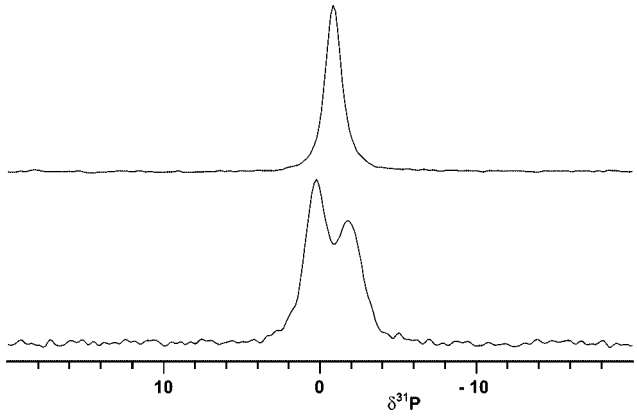


Figure 1. Isotropic line of the solid state CP/MAS ^{31}P NMR spectrum of **6a** at a spinning speed of 13.2 kHz recorded with high-power proton decoupling (top trace) and frequency-shifted Lee–Goldburg decoupling[9] (bottom trace) to suppress homonuclear dipolar coupling between protons. As the decoupling sequence scales the heteronuclear coupling by a factor of 0.577, the observed splitting of 289 Hz corresponds to a value of $^1J_{PH}$ = 501 Hz.

The above results allow to conclude that the reaction of **2** with salicylic aldehyde involves a "normal" hydrophosphanation as the key step. The same regioselectivity was observed in the acid-catalyzed reaction of **2** with 2,3-dihydroxybenzaldehyde (**3b**). NMR studies allowed in this case the direct detection of a small amount of the α-phosphanyl-carbinol **4b** and two further intermediates. The constitution of the latter was assigned as diastereomeric phosphonium salts **7b**, **7′b** by 2D NMR studies, and dynamic exchange between all four species was established by a 2D ^{31}P EXSY NMR spectrum. All products were eventually converted into the phosphane oxide **5b** which was isolated after work-up and characterized by analytical and spectroscopic data. Species similar to **7b**, **7′b** have previously been obtained by reaction of diphenylphosphane (**2**) with formaldehyde in the presence of strong acids.[1,8]

The reaction of **2** with 4-hydroxybenzaldehyde (**3c**) affords as primary product the α-phosphanyl-carbinol **4c** which was isolated by precipitation from methanol and characterized by ^{31}P CP/MAS NMR and analytical data. Key to the structural assignment was the observation of a single resonance ($\delta^{31}P$ = –7.2) which appears at somewhat higher field than that of **6a** and shows no splitting due to $^1J_{PH}$ coupling. In contrast to the elusive 2-hydroxy-substituted carbinol **4a**, the signal of **4c** is also observable in solution ^{31}P NMR spectra although in these solutions, even in the absence of additional acid, partial decomposition to **2** and **3c** occurs (obviously the acidity of the phenolic OH moiety is sufficient to promote an auto-catalytic reaction). Acidic catalysts promote the complete conversion to phos-

phane oxide **5c**. The same behavior can be observed in the reaction of **2** with 3,4-dihydroxybenzaldehyde (**3d**) which affords **5d** as final product. Both **5c** and **5d** were isolated after work-up and characterized by analytical and spectroscopic data.

Finally, the acid-catalyzed reaction of **2** with 3-hydroxybenzaldehyde (**3e**) gives a mixture of dynamically exchanging products the structures of which were assigned to the phosphanyl-carbinol **4e** and the diastereomeric phosphonium salts **7e/7e′** on the basis of a comparison of the observed ^{31}P chemical shifts with those of the products of the previously described reactions. A 1:1 mixture of **7e/7e′** precipitated from the reaction solution and was isolated by filtration. The constitution was confirmed by analytical data; a slow-spinning technique ^{31}P CP/MAS NMR spectrum shows the presence of two isotropic signals of equal intensity with negligible chemical shielding anisotropy. The precipitate dissolved again when the mixture was stirred for prolonged reaction times, and ^{31}P NMR studies allowed to detect the formation of the phosphane oxide **5e** as final product which eventually precipitated from the solution and was characterized by spectroscopic data.

In summary it can be stated that the reactions of the phosphane **2** with hydroxybenzaldehydes **3a**–**e** proceed via hydrophosphanation to yield α-phosphanyl-carbinols **4a**–**e** as initial products. These species are in dynamic equilibrium with the starting materials and phosphonium salts **7** resulting from acid-promoted reaction with further aldehyde. The composition of the equilibrium mixtures depends on the substitution pattern of the aldehydes and lies for **3a**–**d** which feature at least one OH substituent in 2- or 4-position largely on the side of the starting materials, whereas for **3e** the formation of the phosphonium salts **7e**,**e′** appears to be favored. As a consequence, the equilibrium concentration of the adducts **4a**–**e** is rather low, or these species may not be detectable at all. The reduced stability of the adducts with respect to the starting materials is attributable to the electron-releasing nature of the additional hydroxy-substituents which should render the aldehydes weaker electrophiles and the attack by the nucleophilic phosphane energetically less favorable. Aldehydes with 2-hydroxy substituents such as **3a**,**b** may further benefit from additional stabilization by strong intramolecular hydrogen bonding. The observation that all primary adducts may eventually rearrange quantitatively to the corresoponding phosphane oxides **5a**–**e** suggests that the latter are thermodynamically much more stable so that the isomerization is practically irreversible. The easy occurrence of this rearrangement is presumably also facilitated by the stabilization of the resulting transient intermediates by the electron-releasing phenolic OH substituents.

Deoxygenation of the phosphane oxides **4a**–**e** is readily achieved by adaptation of an established procedure[10] involving quaternization of the phosphane oxide moiety with methyl iodide and subsequent reduction with $LiAlH_4$ (Scheme 3). No special protection of the phenol groups is necessary, however, the use of a sufficient excess of the hydride to achieve complete deprotonation of the acidic OH groups is mandatory to obtain reasonable yields of products. Aqueous work-up of the reaction mixture and purification of the crude products by column chromatography affords the phosphanes **8a**–**d** as colorless, moderately oxygen-sensitive solids that were characterized by analytical and spectroscopic data.

Conclusions

It has been confirmed that the reaction of diphenylphosphane with phenolic aldehydes is initiated by reversible formation of α-phosphanyl-carbinols. The presence of OH groups in *p*- or *o*-position appears to destabilize the adducts relative to the starting materials, thus keeping their concentration in the equilibrium mixtures low. The initial adducts rearrange easily to afford isomeric phosphane oxides which may further be reduced to the corresponding phosphanes. The overall reaction sequence permits to access the first alkylphosphane derivatives with tethered catechol and phenol moieties from readily available starting materials and without the necessity of additional efforts for the protection and deprotection of the reactive OH groups. This procedure constitutes a substantial improvement over previously known synthetic protocols which required often more complicated approaches.[4,11] The utilization of this procedure should prove useful for the preparation of functional phosphanes in applications as chelating ligands or supramolecular building blocks.

Experimental Section

General Remarks: Manipulations were carried out under dry argon and solvents were dried by standard procedures if required. Solution NMR spectra were recorded at 30 °C on Bruker Avance 400 (^1H: 400.1 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) or AC 250 spectrometers (^1H: 250 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) at 303 K; chemical shifts are referenced to ext. TMS (^1H, ^{13}C) or 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P). Solid state MAS NMR spectra were recorded on a Bruker Avance 400 instrument with spinning rates between 3 and 14 kHz. Cross polarization with a ramp-shaped contact pulse and mixing times between 3 and 5 ms was used for signal enhancement. MAS NMR spectra aiming at the determination of $^1J_{P,H}$ couplings were recorded under frequency-shifted Lee–Goldburg decoupling of homonuclear proton–proton interactions[9] which scales the visible splitting by a factor of 0.577. All coupling constants are given as absolute values; prefixes *i*, *o*, *m*, *p* denote phenyl ring positions of *P*-C_6H_5 substituents. The resonances of OH protons were not always detectable, presumably as a consequence of chemical exchange, and data are not listed when unequivocal assignment was unfeasible. MS: Varian MAT 711, EI, 70 eV. Elemental analyses: Perkin–Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries.

General Procedure for the Synthesis of Phenol-Functionalized Phosphane Oxides: Diphenylphosphane **2** (12 mmol) was added to a solution of the appropriate aldehyde **3a**–**e** (12 mmol) in DME (10 mL). The solution was stirred for five minutes at room temperature. A catalytic amount of *p*-toluenesulfonic acid (approx. 3–6 mmol) was added and the stirring continued for 48 h. The color-

less precipitate formed was isolated by filtration, washed twice with 5 mL of DME, and dried in vacuo for 4 h.

2-[(Diphenylphosphinoyl)methyl]phenol (5a): Yield 2.59 g (70%); m.p. 177 °C; elemental analysis: $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02 H 5.56, found C 73.90 H 5.37. Spectroscopic data are identical with the values reported in the literature.[7]

3-[(Diphenylphosphinoyl)methyl]benzene-1,2-diol (5b): Yield 3.31 g (85%); m.p. 194 °C; elemental analysis: $C_{19}H_{17}O_3P$ (324.32): calcd. C 70.37 H 5.28; found C 70.44 H 5.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.2 (br., 2 H, OH), 7.74 (m, 4 H, *o*-H), 7.58 (m, 2 H, *p*-H), 7.50 (m, 4 H, *m*-H), 6.81 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, $^6J_{PH}$ = 1.7 Hz, 1 H, H-6), 6.63 (dt, $^3J_{HH}$ = 8.0 Hz, $^5J_{PH}$ = 0.9 Hz, 1 H, H-5), 6.34 (dddm, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, $^4J_{PH}$ = 1.7 Hz, 1 H, H-4), 3.73 (d, $^2J_{PH}$ = 12.8 Hz, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.2 (d, J_{PC} = 2.7 Hz), 143.9 (d, J_{PC} = 4.2 Hz), 133.2 (d, J_{PC} = 2.7 Hz, *p*-C), 131.6 (d, J_{PC} = 9.6 Hz, *o*-C), 130.9 (d, J_{PC} = 100.4 Hz, *i*-C), 129.4 (d, J_{PC} = 12.1 Hz, *m*-C), 122.9 (d, J_{PC} = 6.3 Hz), 121.7 (d, J_{PC} = 1.9 Hz), 119.9 (d, J_{PC} = 8.4 Hz), 114.6 (d, J_{PC} = 2.5 Hz), 35.6 (d, J_{PC} = 67.1 Hz, CH_2) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 40.4 (s) ppm. MS (EI = 70 eV): *m*/*z* (%) = 324.1 (100) [M^+]; 202.1 (38) [Ph_2POH^+], 201 (54) [Ph_2PO^+].

4-[(Diphenylphosphinoyl)methyl]phenol (5c): Yield 2.22 g (60%); m.p. 223 °C; elemental analysis: $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02 H 5.56; found 74.19 H 5.82. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.2 (br., 1 H, OH), 7.76 (m, 4 H, *o*-H), 7.57 (m, 2 H, *p*-H), 7.49 (m, 4 H, *m*-H), 6.82 (m, 2 H, C_6H_4), 6.56 (m, 2 H, C_6H_4), 3.62 (d, $^2J_{PH}$ = 12.2 Hz, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 156.9 (d, J_{PC} = 1.7 Hz), 132.7 (s), 131.8 (d, $^2J_{PC}$ = 9.2 Hz, *o*-C), 131.6 (d, J_{PC} = 4.8 Hz), 129.3 (d, $^3J_{PC}$ = 11.7 Hz, *m*-C), 128.6 (d, J_{PC} = 99.6 Hz), 120.7 (d, J_{PC} = 7.5 Hz), 117.0 (d, J_{PC} = 2.1 Hz), 37.4 (d, J_{PC} = 72.1 Hz, CH_2) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 32.2 (s) ppm.

4-[(Diphenylphosphinoyl)methyl]benzene-1,2-diol (5d): Yield 3.50 g (90%); m.p. 192 °C; elemental analysis: $C_{19}H_{17}O_3P$ (324.32): calcd. C 70.37 H 5.28; found C 69.98 H 5.17. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.47 to 7.23 (m, 10 H, C_6H_5), 6.53 (s, 1 H, C_6H_3), 6.31 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, C_6H_3), 6.12 (d, $^3J_{HH}$ = 8.1, 1 H, C_6H_3), 3.42 (d, $^2J_{PH}$ = 12.9 Hz, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (62 MHz, $CD_3CN/CDCl_3$): δ = 143.8 (d, J_{PC} = 2.3 Hz), 143.2 (d, J_{PC} = 3.1 Hz), 131.7 (d, J_{PC} = 1.8 Hz, *p*-C), 130.3 (d, J_{PC} = 9.4 Hz, *o*-C), 128.1 (d, J_{PC} = 11.7 Hz, *m*-C), 126.9 (d, J_{PC} = 101.8 Hz, *i*-C), 121.2 (d, J_{PC} = 6.1 Hz), 120.9 (d, J_{PC} = 8.4 Hz), 116.6 (d, J_{PC} = 4.8 Hz), 114.4 (d, J_{PC} = 2.3 Hz), 35.1 (d, J_{PC} = 68.2 Hz) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 40.4 (s) ppm.

3-[(Diphenylphosphinoyl)methyl]phenol (5e): Yield 2.22 g (60%); m.p. 198 °C; elemental analysis: $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02 H 5.56; found C 74.10 H 5.60. ^{1}H NMR (250 MHz, $CD_3CN/CDCl_3$): δ = 7.55 (m, 4 H, *o*-H), 7.40 to 7.25 (m, 6 H, *m*/*p*-H), 6.80 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, H-5), 6.59 (s, 1 H, H-2), 6.44 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, H-4/6), 6.41 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, H-4/6), 3.50 (d, $^2J_{PH}$ = 13.4 Hz, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (62 MHz, $CD_3CN/CDCl_3$): δ = 157.1 (d, J_{PC} = 2.6 Hz), 132.4 (d, J_{PC} = 2.9 Hz, *p*-C), 131.2 (d, J_{PC} = 9.5 Hz, *o*-C), 131.0 (s), 130.9 (d, J_{PC} = 102.3 Hz, *i*-C), 129.5 (d, J_{PC} = 2.1 Hz), 128.9 (d, J_{PC} = 11.8 Hz, *m*-C), 121.8 (d, J_{PC} = 5.8 Hz), 117.5 (d, J_{PC} = 5.0 Hz), 114.2 (d, J_{PC} = 2.9 Hz), 37.1 (d, J_{PC} = 67.1 Hz) ppm. ^{31}P{^{1}H}NMR (101 MHz, $CDCl_3$): δ = 31.4 ppm.

2-[(Diphenylphosphanyl)hydroxymethyl]phenol Hydrochloride (6a): 2-Hydroxybenzaldehyde (**3a**) (0.64 mL, 6 mmol) was added to a solution of diphenylphosphane **2** (1.05 mL, 6 mmol) in diethyl ether (10 mL). This mixture was stirred for five minutes at room temperature and an excess of conc. hydrochloric acid (2 mL, 24 mmol) was added. A colorless precipitate formed immediately. The reaction mixture was then stirred for further 60 min, the precipitate filtered off, washed twice with diethyl ether (5 mL), and dried for 1 h in vacuo. Yield: 1.86 g (90%); m.p. 104 °C; elemental analysis: $C_{19}H_{18}ClO_2P$ (344.78): calcd. C 66.19 H 5.26 Cl 10.28; found C 66.76 H 5.38 Cl 8.54. ^{31}P{^{1}H}NMR (solid, 162 MHz, CP/MAS): δ_{iso} = –0.8.

4-[(Diphenylphosphanyl)hydroxymethyl]phenol (4c): A solution of diphenylphosphane (**2**) (1.43 mL, 8.2 mmol) and 4-hydroxybenzaldehyde (**3c**) (1.00 g, 8.2 mmol) in methanol (10 mL) was stirred for 5 min at room temperature and conc. hydrochloric acid (0.25 mL, 3 mmol) was added. A colorless precipitate formed immediately. The reaction mixture was stirred for further 60 min, the precipitate filtered off and dried for 1 h in vacuo. Yield: 2.27 g (90%); m.p. 168 °C; elemental analysis: $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02 H 5.92; found 74.29 H 5.92. ^{31}P NMR (101 MHz, THF): δ = –2.3 (s) ppm. ^{31}P{^{1}H}NMR (solid, 162 MHz, CP/MAS): δ_{iso} = –7.2 ppm.

Bis[hydroxy(3-hydroxyphenyl)methyl]diphenylphosphonium Toluenesulfonate (7e/7e′): A solution of diphenylphosphane (**2**) (1.43 mL, 8.2 mmol) and 3-hydroxy benzaldehyde (**3e**) (1.00 g, 8.2 mmol) in DME (5 mL) was stirred for 5 min at room temperature and *p*-toluenesulfonic acid (0.60 g, 3.2 mmol) was added. A colorless precipitate began to form after 10 min. The reaction mixture was stirred for 12 h, the precipitate filtered off, washed twice with DME, and dried for 4 h in vacuo. Yield: 1.73 g (90%); m.p. 121 °C; elemental analysis: $C_{33}H_{31}O_7PS$ (602.64): calcd. C 65.77 H 5.19; found 65.39 H 5.30. ^{31}P{^{1}H}NMR (solid, 162 MHz, CP/MAS): δ_{iso} = 30.5, 29.9 ppm.

General Procedure for the Synthesis of Phenol-Functionalized Phosphanes: The appropriate phosphane oxide **5a**–**d** (10 mmol) was dissolved in dry THF (100 mL). Methyl iodide (0.69 mL, 11 mmol) was added via a syringe and the solution stirred for 2 h at room temperature. The mixture was then cooled to 0 °C and solid $LiAlH_4$ (1.7 g, 45 mmol) added in several small portions. The reaction mixture was warmed to ambient temperature, and stirring was continued for another 5–6 h. The progress of the reaction was monitored by TLC. The reaction flask was again cooled to 0 °C, and 50 mL of 1 M hydrochloric acid were added in several portions (the first few drops had to be added very carefully until the exothermic reaction became less violent). The organic layer was separated and the aqueous layer washed with ethyl acetate (3 × 50 mL). The combined organic phases were dried overnight with Na_2SO_4 and all volatiles evaporated in vacuo. The crude products were purified by column chromatography (silica, petroleum ether:ethyl acetate = 7:3).

2-[(Diphenylphosphanyl)methyl]phenol (8a): Yield 1.81 g (62%); colorless oil, elemental analysis: $C_{19}H_{17}OP$ (292.32): calcd. C 78.07 H 5.86; found C 74.33 H 5.91. ^{1}H NMR (250 MHz, [D_8]toluene): δ = 6.8 to 7.5 (m, 10 H, C_6H_5), 6.80 (t, 1 H, $^3J_{HH}$ = 7.7 Hz), 6.74 (d, 1 H, $^3J_{HH}$ = 7.7 Hz), 6.61 (d, 1 H, $^3J_{HH}$ = 7.8 Hz), 6.50 (t, 1 H, $^3J_{HH}$ = 7.5 Hz), 3.32 (s, 2 H, CH_2) ppm. ^{31}P{^{1}H} NMR (101 MHz, [D_8]toluene): δ = –15.0 ppm. The ^{1}H NMR spectroscopic data match those published earlier.[11]

3-[(Diphenylphosphanyl)methyl]benzene-1,2-diol (8b): Yield 1.85 g (60%); m.p. 82 °C; elemental analysis: $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02 H 5.56; found C 73.91 H 5.73. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 to 7.30 (m, 10 H, C_6H_5), 6.78 (dm, $^3J_{HH}$ = 7.9 Hz, 1 H, C_6H_3), 6.64 (tm, $^3J_{HH}$ = 7.9 Hz, 1 H, C_6H_3), 6.43 (dm, $^3J_{HH}$ = 7.9 Hz, 1 H, C_6H_3), 6.02 (br., 1 H, OH), 5.86 (br., 1 H, OH), 3.52 (d, $^2J_{PH}$ = 1.7 Hz, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 145.0 (d, J_{PC} = 1.6 Hz), 141.7 (d, J_{PC} = 3.7 Hz), 132.8

(d, $^3J_{PC}$ = 17.4 Hz, *m*-C), 130.9 (d, $^2J_{PC}$ = 9.5 Hz), 129.3 (s, *p*-C), 128.9 (d, $^3J_{PC}$ = 12.1), 128.6 (d, J_{PC} = 7.4 Hz, *o*-C), 122.4 (d, J_{PC} = 6.3 Hz), 121.0 (d, J_{PC} = 1.6 Hz), 113.6 (d, J_{PC} = 2.6 Hz), 30.7 (d, $^1J_{PC}$ = 10.5 Hz, CH_2) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = –13.1 (s) ppm. MS (EI = 70 eV): *m*/*z* (%) = 308.1 (100) [M^+], 186.1 (45) [Ph_2PH^+], 185.1 (44) [Ph_2P^+], 183.0 (54) [Ph_2P^+–H_2], 123.1 (45) [M^+–PPh_2], 108.1 (54).

4-[(Diphenylphosphanyl)methyl]benzene-1,2-diol (8d): Yield 2.16 g (70%); m.p. 144 °C; elemental analysis: $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02 H 5.56; found C 74.06 H 5.59. ^{1}H NMR (400 MHz, [D_8]-THF): δ = 7.68 (s, 1 H, OH), 7.53 (s, 1 H, OH), 7.41 (m, 4 H, *o*-H), 7.33 to 7.25 (m, 6 H, *m*/*p*-H), 6.58 (dd, $^4J_{HH}$ = 1.7 Hz, $^4J_{PH}$ = 1.7 Hz, 1 H, C_6H_3), 6.52 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, C_6H_3), 6.38 (dm, $^3J_{HH}$ = 8.0 Hz, 1 H, C_6H_3), 3.31 (s, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D_8]THF): δ = 145.6 (d, J_{PC} = 1.5 Hz), 144.2 (d, J_{PC} = 2.9 Hz), 139.9 (d, J_{PC} = 16.8 Hz, *i*-C), 133.3 (d, J_{PC} = 18.7 Hz, *m*-C), 129.1 (d, J_{PC} = 8.8 Hz), 128.7 (s, *p*-C), 128.6 (d, J_{PC} = 6.3 Hz, *o*-C), 120.9 (d, J_{PC} = 7.1 Hz), 116.7 (d, J_{PC} = 7.6 Hz), 115.3 (d, J_{PC} = 1.5 Hz), 35.6 (d, J_{PC} = 15.1 Hz) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = –10.4 ppm. MS (EI = 70 eV): *m*/*z* (%) = 308.1 (48) [M^+], 186.1 (38) [Ph_2PH^+], 183.0 (27) [Ph_2P^+–H_2], 123.1 (100) [M^+–PPh_2], 108.1 (27).

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