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Conversion of Dibenzoxaphosphinines into 2-Hydroxybiphenyl-2′-ylphosphane Ligands and Their BH_3 Adducts: The O–$H^{\delta+}$···$H^{\delta-}$–B Hydrogen–Hydrogen Bond

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Chlorodibenz[*c*,*e*][1,2]oxaphosphinine $\mathbf{1_{Cl}}$ reacted with bulky organolithium compounds R^1Li (R^1 = *t*Bu, mesityl) under mild conditions to yield organodibenz[*c*,*e*][1,2]oxaphosphinines $\mathbf{1_R}^1$, which underwent ring-opening metathesis with less bulky organolithium compounds R^2Li. After *O*-trimethylsilylation, 2-(trimethylsilyloxy)biphenylylphosphanes **2** were isolated. Reaction of $\mathbf{1_{Cl}}$ with R^2Li followed by silylation provided symmetrically *P*-substituted compounds **2**. The formation of compounds **3** and **4** demonstrated the facile hydrolysis and oxidation of $\mathbf{1_R}^1$, the formation of compound $\mathbf{5c_{ox}}$ indicated the sensitivity of **2** to hydrolysis and air oxidation. Methanolysis of **2** provided the free hydroxybiphenylylphosphanes **5** (for further modification by *O*-acylation), which were converted into air-stable borane adducts **6**. The latter were unable to undergo *O*-acylation. Acylation of **5** followed by borane protection afforded *O*-acyloxybiphenylylphosphane–borane adducts, as demonstrated by the formation of compounds **7a** and **8a**. X-ray crystal structure analyses revealed intermolecular O–H···H–B hydrogen–hydrogen bonds; for compound **6b** the average H···H distance is 1.90 Å, whereas for **6e** a three-centre O–H···H_2B interaction (av. H···H 2.25 Å) was observed, which is still shorter than twice the van der Waals radius for hydrogen (2.4 Å). To the best of our knowledge this is the first report on hydrogen–hydrogen bonds in functionally substituted phosphane–boranes and may explain the low reactivity at the OH group. Only on stronger heating was hydrogen evolved.

Introduction

Among the wide variety of ligands studied in transition-metal catalysis, biarylylphosphanes have attracted considerable interest in the last decade. Various applications with several different transition metals have been studied, but the most striking results were obtained with palladium catalysts with bulky and basic dialkylphosphanyl derivatives, which provide greatly improved activity in a large number of carbon–carbon and carbon–heteroatom coupling reactions. Additional substituents, including alkoxy or amino donor groups, at the *ortho* position of the adjacent aryl group were found to improve the performance of these catalysts further.[1,2] 2-Hydroxybiarylylphosphanes[3–10] have received much less attention in this respect. Axial chiral 2-hydroxybinaphthylylphosphanes[3] are useful organocatalysts in the asymmetric aza-Morita–Baylis–Hillman reaction as a result of the concomitant action of the nucleophilic phosphanyl group and a hydrogen-bonding motif.[4] However, the effect of the *o*-hydroxy group on biarylylphosphane-based transition-metal catalysts has only been sparingly investigated and proved to be variable. We observed blockage of the hydrogenation activity of Rh complexes under mild conditions but tolerance and high-yielding Rh-catalysed hydroformylation of vinyl and allyl acetate under pressure and at an elevated temperature.[5] The OH group has also been used to couple biarylylphosphane ligands to soluble polymer supports to provide efficient palladium catalysts for the Suzuki–Miyaura coupling of aryl chlorides,[6] to resolve racemic 2-hydroxybinaphthylylphosphanes by column chromatography of diastereoisomeric *O*-camphorsulfonates[7] and to synthesize asymmetric *O*-camphanoyl derivatives, which, after enantiomer separation by crystallization, allowed Rh-catalysed hydrogenation of *N*-(1-phenylvinyl)acetamide with excellent yields and moderate *ee*s.[8] Coupling with chlorodibenzoxaphosphorinane gave a biphenylylphosphanylphosphinite ligand that formed a stable *P*,*P*-chelate $PtCl_2$ complex.[9a] Stable chiral *O*-phosphite derivatives, valuable ligands for hydroformylation catalysts, have so far been synthesized by stereoselective reduction of asymmetric 2-hydroxybiarylylphosphane oxides.[11] A potential alternative route to asymmetric derivatives is the diastereoselective *O*-acylation of 2-hydroxybiphenylylphosphanes with asymmetric electrophiles, which provides suf-

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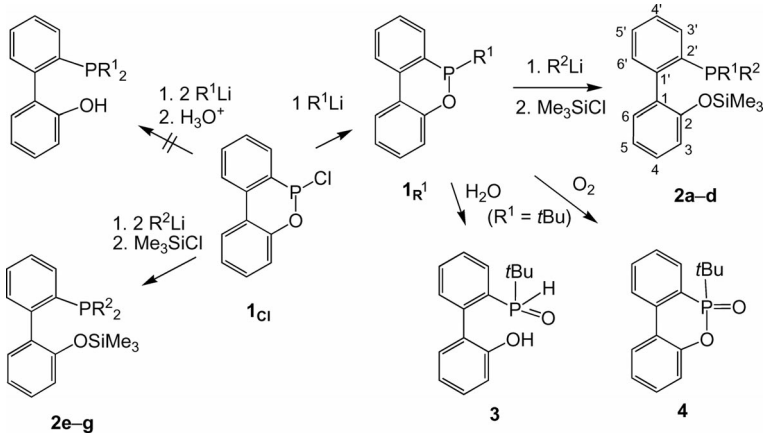
ficient steric bulk to prevent rotation around the C–C axis, whereas this still occurs in the 2-hydroxy derivatives. As a first step in this direction we have begun to study bulkily substituted 2-hydroxybiphenylylphosphanes and the protection of air-sensitive derivatives by complexation with BH_3. Surprisingly, the reactivity of the hydroxy group was strongly diminished. We report here on the synthesis of these compounds and the detection of B–H···H–O hydrogen–hydrogen bonds.

Results and Discussion

Synthesis

For the synthesis of 2-hydroxybiarylylphosphanes three routes have been established: (i) the monophosphinoylation of BINOL triflates with diorganophosphane oxides followed by hydrolysis and reduction of the phosphinoyl group, usually used for axial chiral derivatives,[3,4] (ii) ether cleavage of dibenzo- or dinaphthofuran with lithium in THF and coupling with chlorodiorganophosphanes,[5–7] (iii) reaction of chlorodibenzoxaphosphinine **1$_{Cl}$** with excess Grignard reagent.[9,10] In a patent, coupling of **1$_{Cl}$** with organolithium compounds has been claimed.[12] Although phenols, alcohols and amines allow selective monosubstitution of benzo- or naphtho-annulated chloro-1,2-oxaphosphinines to yield catalytically valuable heterocyclic annulated oxaphosphinine ligands,[13–15] reactions with organometallic reagents seem to be less selective. Phenylmagnesium bromide and **1$_{Cl}$** gave a mixture of mono- and disubstituted products; only the bulky 2,4,6-triisopropylphenylmagnesium bromide underwent clean monosubstitution.[9b] We supposed that the increased reactivity of organolithium compounds compared with Grignard compounds would force disubstitution and allow the synthesis of 2-hydroxybiphenylylphosphanes with bulky substituents at the phosphorus atom and decided to follow this fourth route. However, several attempts to prepare di-*tert*-butyl(2-hydroxybiphenylyl)phosphane by the reaction of **1$_{Cl}$** with excess *tert*-butyllithium (up to 2.5 equiv.) and subsequent workup by treatment with acid (aqueous H_2SO_4) or by *O*-trimethylsilylation failed. Only mixtures were obtained in diethyl ether or THF or under forced conditions at an elevated temperature in toluene or xylene. Similarly, an attempt to convert **1$_{Cl}$** with 2 equiv. of mesityllithium did not lead to the expected (hydroxybiphenylyl)dimesitylphosphane in toluene/diethyl ether at room temperature. Under mild conditions – slow addition of R^1Li and low temperature – controlled monosubstitution took place and furnished the *tert*-butyl- and mesityldibenzoxaphosphinines **1$_{tBu}$** and **1$_{Mes}$**, respectively, in good yields. Excess organolithium reagent, necessary to complete substitution of chloride (monitored by NMR), was scavenged by reaction with chlorotrimethylsilane. The products were purified by vacuum distillation. An attempt to introduce a second *tert*-butyl group at the phosphorus atom by heating a solution of **1$_{tBu}$** and *t*BuLi in toluene under microwave irradiation (6 min, 100 W, ca. 100 °C) led to partial conversion of **1$_{tBu}$** (<40%) and the formation of a mixture. The main product after *O*-trimethylsilylation displays a ^{31}P NMR signal at δ = 21.5 ppm, but was neither obtained in the pure form nor identified. More satisfactory were the conversions of dibenzoxaphosphinines **1$_{tBu}$** and **1$_{Mes}$** with less bulky organolithium reagents R^2Li such as methyl- or *p*-tolyllithium, although they too needed controlled reaction conditions to provide defined products. Whereas treatment of **1$_{tBu}$** with methyllithium at room temperature or at –30 °C gave mixtures of products, addition at –90 °C and slow warming to 20 °C led to clean ring-opening metathesis. The resulting lithium 2-oxybiphenylylphosphanes, which display broad phosphorus resonances in the ^{31}P NMR spectra, were silylated with excess chlorotrimethylsilane to afford the silyloxybiphenylylphosphanes **2a**,**b** (Scheme 1). The compounds were easily separated from LiCl and unconsumed $ClSiMe_3$ and purified by high-vacuum distillation to give yields of about 60%. Both compounds displayed two sharp phosphorus signals, which indicates a sufficiently high barrier to rotation around the C–C axis to generate two pairs of diastereoisomers (ca. 93:7 for **2a** and ca. 60:40 for **2b**). Analogous conversion of **1$_{Mes}$** with methyllithium and subsequent silylation provided **2c**



Scheme 1. Conversion of dibenzoxaphosphinine **1$_{Cl}$** to **1$_{R^1}$** and to (trimethylsilyloxy)biphenylylphosphanes **2**: R^1 = *t*Bu, R^2 = Me (**a**) and *p*Tol (**b**); R^1 = mesityl, R^2 = Me (**c**); R^1 = mesityl, R^2 = *t*Bu (**d**); $2R^2$ = Me (**e**), 2-anisyl (**f**), 2,4-dimethoxyphenyl (**g**).

in 67% yield with a diastereoisomer ratio of around 1:1. The ring-opening reaction of $\mathbf{1_{Mes}}$ with the bulky but highly reactive *t*BuLi proceeded nearly quantitatively in THF by addition at a very low temperature and slow warming (–100 to 20 °C), as indicated by a broad phosphorus resonance at δ = –3.5 ppm. Subsequent silylation gave around 80% crude **2d** (by ^{31}P NMR spectroscopy), isolated in 40% yield after high-vacuum distillation (diastereoisomer ratio ca. 1:1). The alternative route, reaction of the bulky $\mathbf{1_{tBu}}$ with the less reactive mesityllithium and silylation, failed to give this compound. Attempts to induce enantioselective ring-opening metathesis of $\mathbf{1_{tBu}}$ with MeLi or *p*TolLi in the presence of (–)-sparteine to select one of the two asymmetric phosphane configurations failed. The diastereoisomer ratio remained unchanged.

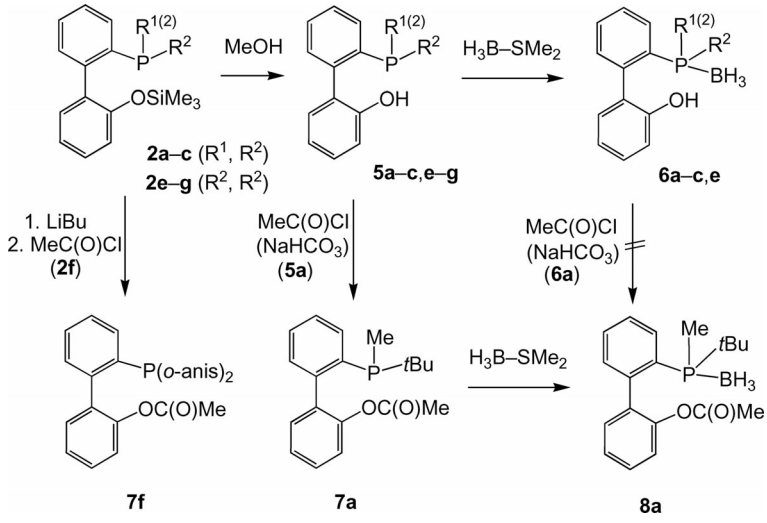
For comparison, and to lower the number of isomers after *O*-acylation with chiral acids,[8] the reactivity of $\mathbf{1_{Cl}}$ towards some less bulky organolithium compounds R^2Li was studied. Treatment with 2 equiv. of methyllithium, 2-methoxy- or 2,4-dimethoxyphenyllithium led to substitution of the chloride and ring-opening metathesis to give, after treating the lithium salts with excess $ClSiMe_3$, the 2-(trimethylsilyloxy)biphenylylphosphanes **2e**–**g**. NMR analyses showed analogous behaviour for phenyllithium. After hydrolysis, the phosphorus resonance (δ^{31}P = –12.1 ppm) of the known 2-hydroxybiphenyl-2′-yldiphenylphosphane[9] was observed. ^{31}P NMR monitoring of the conversion of $\mathbf{1_{Cl}}$ with *p*-tolyllithium in a 1:1 molar ratio showed that the reaction of non-bulky lithium reagents did not proceed selectively to $\mathbf{1_R^2}$ by substitution of chlorine but resulted in a mixture of mono- and disubstituted products (δ = 84.0, –13.3, –15.3 ppm). It may be reasoned that after replacement of chlorine by an organic substituent the basicity of oxygen is increased and coordination of LiR favoured, which then leads to competing reactions at the P–O bond of $\mathbf{1_R^2}$ and partial disubstitution, as also observed in reactions of $\mathbf{1_{Cl}}$ with PhMgBr in a 1:1 molar ratio.[9b]

Reactivity

The dibenzoxaphosphorinanes **1** are sensitive to hydrolysis and air oxidation. For compound $\mathbf{1_{tBu}}$ hydrolysis resulted in the secondary phosphane oxide **3**, whereas oxidation furnished the cyclic phosphinate **4**. The ^{31}P NMR spectra display similar chemical shifts for the major and minor diastereoisomers of **3** (δ = 43.8 and 58.9 ppm) and for **4** (δ = 45.3 ppm), but the compounds can easily be distinguished by the large $^1J_{PH}$ coupling constant for **3** in the proton-coupled phosphorus NMR spectrum, which is lacking in **4**. Detailed structural information on **3** has been provided by a crystal structure analysis (see below).

Hydrolysis or methanolysis of the 2-(trimethylsilyloxy)biphenylylphosphanes **2** furnished 2-hydroxybiphenylylphosphanes **5** (Scheme 2). Methanolysis was found to be advantageous for product isolation[5] and was therefore preferred. For the alkyl-aryl and dialkyl derivatives **2a**–**c** and **2e**, the reaction proceeded at room temperature and was complete after storage of the solution overnight. For the diaryl derivatives, heating at reflux in methanol was required (1–4 h for **2f**; 1–2 d for **2g**); the low solubility of the products **5f** and **5g** caused them to be deposited in pure form. The synthesis of hydroxybiarylylphosphanes via the silyl ethers and their methanolysis circumvented problems in direct workup with aqueous acids associated with phosphonium or phenolate salt formation if the pH was not optimally adjusted. The ambiphilic behaviour of the phosphanes with phenolic OH groups towards aqueous bases and acids has been studied in more detail for 2-[(alkyl)(phenyl)phosphanyl]-phenols.[16]

The *P*-alkyl-*P*-aryl- and *P*,*P*-dialkyl-substituted trimethylsilyloxy- and hydroxybiphenylylphosphanes were oxidized in air to varying extents to form the corresponding phosphane oxides. Thus, **5a** in ethereal solution was completely oxidized on contact with air overnight, as indicated by ^{31}P NMR monitoring ($\mathbf{5a_{Ox}}$: δ = 57.6 and 53.1 ppm). Detailed



Scheme 2. Formation of 2-hydroxybiphenylylphosphane–boranes **6a**–**c**,**e** and **8a**.

structural information has been provided by an X-ray crystal structure analysis of the phosphane oxide **5c$_{Ox}$** (see below), similarly formed by oxidation of **5c** with air.

An efficient and general method for preventing aerial oxidation of the phosphane ligands is to form the borane adducts. Various functional groups are tolerated,[2,17] even the acidic OH group in 2-phosphanylphenols[18] or the COOH group in 2-(diphenylphosphanyl–borane)propionic acid.[19] BH_3 can be removed by treatment with strong amine bases at room temperature or by heating.[17] For transition-metal catalytic applications that tolerate BH_3 or need it for reduction or as a Lewis acid, the borane adducts can also be used directly, because transition metals usually bind more strongly to phosphane ligands and replace BH_3. Thus, in screening tests of the oligo- or polymerization of ethylene we observed high activity of nickel catalysts, formed in situ from [Ni(1,5-cod)$_2$] and the borane adducts of 2-(diphenyl- or dicyclohexylphosphanyl)phenol, and no marked influence of the borane additive on the selectivity, molecular weight and microstructure of the polymers.[18d] The useful properties of phosphane–boranes prompted us to convert the *P*-alkyl-*P*-aryl- and *P*,*P*-dialkyl-substituted 2-hydroxybiphenylylphosphanes into the borane adducts **6a**–**c** and **6e**. This occurs quantitatively by treatment with a slight excess of $H_3B{\cdot}SMe_2$ in dichloromethane at room temperature. After removal of the volatiles in vacuo, minor contamination by an SMe_2 adduct was observed. Purification was achieved by crystallization from methanol, which gave **6a**, **6b** and **6e** in high yields, whereas attempts to crystallize the compounds from dichloromethane, tetrahydrofuran, diethyl ether, hexane or toluene failed. Ethanol or acetonitrile also allowed crystallization. Compound **6c**, prepared from crude **5c**, could not be obtained in crystalline form and was purified by column chromatography on silica gel to yield a viscous oil. Initial gas evolution on contact with silica gel may be caused by excess $H_3B{\cdot}SMe_2$; the adducts **6** were found to be stable to silica gel. They can be handled in air and stored for months without decomposition; only on stronger heating (130–145 °C) does decomposition occur with evolution of dihydrogen. A disadvantage with respect to *O*-functionalization is that the reactivity of the OH group is also strongly reduced, which seems not to be the case in phosphane–boranes with aliphatic hydroxy groups. These are known to undergo various reactions.[2,17] Attempts at esterification of **6a** with the highly reactive acetyl chloride failed under various conditions, in diethyl ether at room temperature or in THF at reflux in the presence of anhydrous $NaHCO_3$ or $KHCO_3$ to trap HCl and unconverted phenolate. Acetylation of **5a** with CH_3COCl/$NaHCO_3$ to give **7a** (68% yield), and subsequent reaction with $H_3B{\cdot}SMe_2$ in dichloromethane was necessary to obtain 2-acetoxybiphenylylphosphane–borane **8a**. A possible explanation for the lower reactivity of the OH group of the phosphane–borane **6a** relative to the unprotected phosphane **5a** is that the negatively charged borane in HO-biaryl-$PR_2^{\delta+}\cdots BH_3^{\delta-}$ favours interactions with the carbonyl group of the acetyl chloride and thus suppresses the usual reaction with the weakly nucleophilic phenol(ate) oxygen atom. For the more nucleophilic aliphatic OH groups the effect will be less pronounced. Support for the donor properties of the coordinated BH_3 group is provided by the short distances between hydrogen atoms of the borane and the hydroxy proton observed in single crystals of **6b** (ca. 1.88 and 1.93 Å, see below), which lie in the normal range of "dihydrogen bonds" (1.75–1.95 Å[20]), and also related close H···H contacts in **6e** (2.24 and 2.26 Å), which are less than twice the van der Waals radius of the hydrogen atom (2.4 Å).

Structural Aspects

The structures of the compounds were determined by multinuclear NMR spectroscopic data, elemental analysis and HRMS and in more detail for **3**, **5c$_{Ox}$**, **6b** and **6e** by X-ray crystal structure analysis. The accordance of the proposed structures with the ^1H and ^{13}C NMR spectroscopic data was confirmed by assignment of the partly superimposed signals in the rather complex spectra of representative compounds of **1**, **2** and **6** and for **7f** through H–H and C–H COSY experiments. C–H COSY spectra of **1$_{Mes}$** and **6b** in the aryl range are depicted in Figures 1 and 2. Apart from the typical upfield region of the phenoxy protons 3-H and 5-H in the spectra of the dibenzoxaphosphinine **1$_{Mes}$**, the carbon doublet with J_{PC} = 23.8 Hz, assigned to C-3′, and the relatively strong downfield shifts of 6-H and 6′-H, despite upfield C-6 and C-6′ carbon signals, are characteristic. The latter is indicative of planar or only slightly twisted biphenyl systems and can be attributed to the steric proximity by fixation through the six-membered P–O ring. After ring-opening, the planes of the biphenyl rings are strongly twisted, which causes considerable upfield shifts of the 6-H and 6′-H signals in compounds of type **2**–**8**.

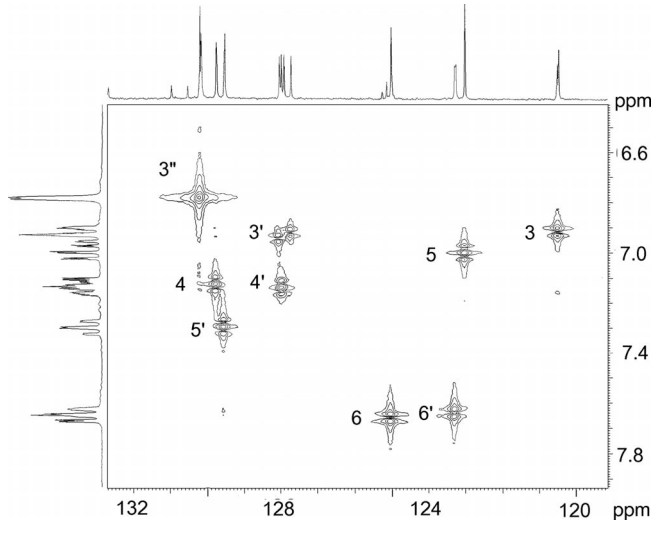


Figure 1. C–H COSY NMR spectrum of **1$_{Mes}$** (aryl range; assignment numbers as shown for compound **2** in Scheme 1; 3′′ for *m*-CH of the mesityl group).

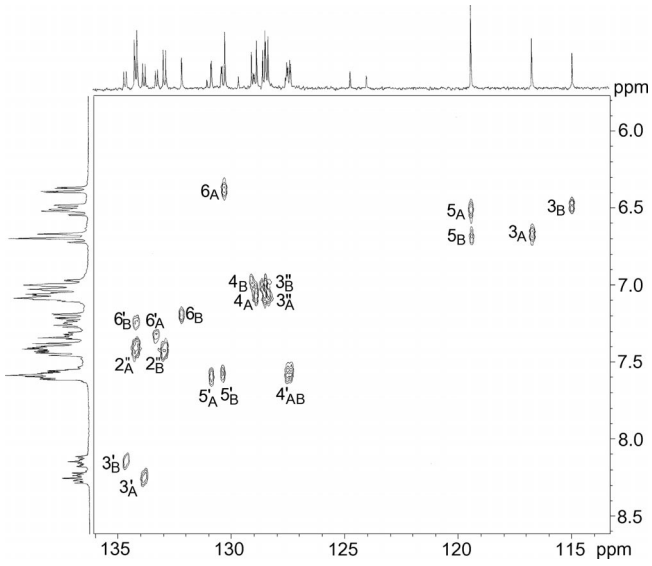


Figure 2. C–H COSY NMR spectrum of **6b** (aryl range).

The P–C coupling constants of the carbon nuclei in the *P*-phenyl ring are not comparable with the rotation-averaged coupling constants of phenylphosphanes but vary strongly for the two *ortho* and *meta* positions of **2**–**8**. For oxybiphenylylphosphanes **2** and **5**, the $^2J_{P\text{-}C1'}$ coupling constants are much larger than $^2J_{P\text{-}C3'}$, and even $^3J_{P\text{-}C6'}$ is somewhat larger, whereas $^3J_{P\text{-}C4'}$ is zero or very small. For the borane adducts **6**, however, $^2J_{P\text{-}C3'}$ is much larger than $^2J_{P\text{-}C1'}$ and $^3J_{P\text{-}C4'}$ is considerably larger than $^3J_{P\text{-}C6'}$. The carbon nuclei C_q-2′ (*ipso* to the phosphorus atom) are clearly distinguished by strongly increased $^1J_{P\text{-}C}$ coupling constants in the spectra of the borane adducts. Finally, it should be mentioned that the 2-hydroxybiphenylylphosphanes **5f** and **5g** with two equal *o*-methoxy-substituted aryl groups display only one broad (**5f**) or sharp (**5g**) phosphorus signal at room temperature. The proton signals, particularly of the dimethoxyphenyl group of **5g**, are strongly broadened, which hints at dynamic processes on the NMR timescale, probably rotation around the P–C bond, interconversion of the two rotamers with the 2-methoxy groups on the same or opposite sides. The protons of the biaryl part appear as sharp multiplets, but the 6-H and in particular the 3′-H signal are strongly shifted upfield in comparison to those of other 2-hydroxybiphenylylphosphanes because of the influence of the *o*-OMe group.

The structures of the 2-hydroxybiphenylylphosphane oxides **3** and $\mathbf{5c_{Ox}}$, formed by (slow) hydrolysis of $\mathbf{1_{tBu}}$ in moist benzene and hydrolysis and air oxidation of **2c**, respectively, were determined by X-ray crystallography. Furthermore, single crystals of the 2-hydroxybiarylylphosphane–boranes **6b** and **6e** were grown, and the resulting crystal structure analyses delivered additional structural information not deducible from the NMR analyses. Common features in both types of compounds are the twisted ring planes of the two connected phenyl rings, typical of biaryl compounds, and the formation of hydrogen bonds between the OH hydrogen atom and the phosphorus substituents, O (in $\mathbf{5c_{ox}}$ through an additional a water molecule; see packing figure in the Supporting Information) or BH_3, which represent classic O···H–O and non-classic B–H···H–O hydrogen bonds, respectively. The P–C, P=O, C–C and C–O bonds have normal bond lengths and angles. The structure determination of the secondary 2-hydroxybiphenylylphosphane oxide **3** (Figure 3) shows it to be a racemate of the diastereoisomer $S_PR_{biphenyl}$ in the solid state, crystallizing in the triclinic space group $P\bar{1}$ as a deuteriobenzene trisolvate. The other diastereoisomer is presumably less stable and converts to the more stable isomer by rotation around the C–C axis. The biphenyl interplanar angle is 68°. Two molecules are connected with an inversion symmetry (see the Supporting Information) by linear hydrogen bonds between the P=O and hydroxy group [D–H···A 172.2(6)°]. In addition, every unit cell contains six molecules of the solvent C_6D_6. The three independent C_6D_6 molecules are connected either to one molecule of **3** through a C–H···π interaction [C3–H3B···Cent(C51–C56) 2.73 Å, normalized] or in a tape of mutually perpendicular molecules (C31–C36 and C41–C46, interplanar angle 72°) parallel to the *a* axis with no short C–H···π contacts (<3 Å) but with incipient face-to-edge or edge-to-edge contacts. There is no ring stacking. The angles around the phosphorus atom range from 102.7(5)° [C1–P–H02] to 113.3(5)° [C1–P–H02] and thus correspond to a slightly distorted tetrahedron.

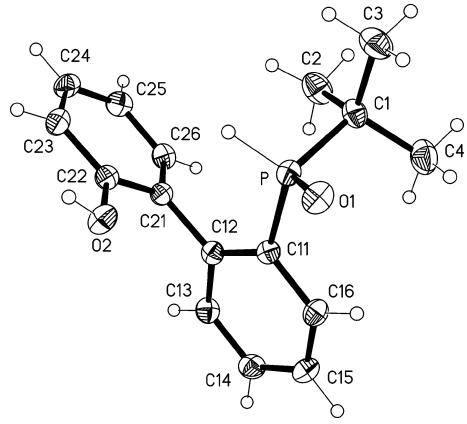


Figure 3. Molecular structure of **3**. Ellipsoids are drawn at the 50% probability level. C_6D_6 molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P–O1 1.5026(9), P–C11 1.8042(13), P–C1 1.8239(14), P–H02 1.28(1); O1–P–C11 111.57(6), O1–P–C1 112.79(6), C11–P–C1 109.11(6)°.

The P-tertiary 2-hydroxybiphenylylphosphane oxide $\mathbf{5c_{ox}}$ (Figure 4) crystallizes as a hemihydrate in the monoclinic space group *C*2/*c*; it is a racemate of the diastereoisomer $S_PS_{biphenyl}$ in the solid state (in solution the C–C rotation barrier is low). The biphenyl interplanar angle is 90°. The water molecule lies with its oxygen on a two-fold axis and connects four molecules of $\mathbf{5c_{ox}}$ through classic hydrogen bonds, two through the 2-hydroxy groups [H···A 1.91(2) Å, D···A 2.6976(13) Å, D–H···A 173(2)°] and two directed towards the O=P group [H···A 1.78(2) Å, D···A 2.6475(13) Å, D–H···A 176(2)°], thus forming hydrogen-bonded tapes parallel to the *c* axis (see the Supporting Information).

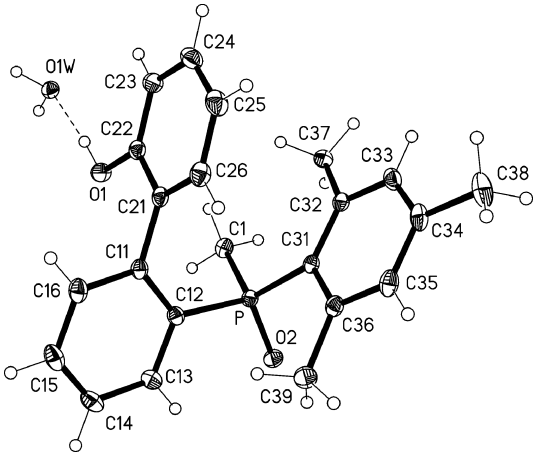


Figure 4. Molecular structure of the *P*-oxide of $\mathbf{5c_{Ox}}$. Ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: P–O 1.5036(10), P–C1 1.7939(14), P–C31 1.8200(13), P–C12 1.8217(13); O2–P–C 109.18–110.60(6), C1–P–C12 103.91(6), C1–P–C31 115.24(6), P–C12–C11 125.17(10), P–C12–C13 115.42(10).

The 2-hydroxybiphenylylphosphane–borane **6b** forms a racemate of the diastereoisomer $R_PR_{biphenyl}$, crystallizing in the orthorhombic space group $Pna2_1$ with one *R*,*R* and one *S*,*S* molecule in the asymmetric unit (Figures 5 and 6). The molecules are very similar, with an r.m.s. deviation of a least-squares fit of 0.02 Å; the biphenyl interplanar angles are both 76°. The P–C bond lengths are similar to those of the related borane-free *tert*-butyl(2-hydroxybiphenylyl)phenylphosphane[5] but the angles C12–P1–C31 and C12–P1–C38 are somewhat larger [105.82(8) and 111.12(10) vs. 101.89(9) and 103.18(10)°], because the BH_3 substituents have replaced the lone-electron pairs. The P–B bonds of **6b** are slightly longer than in $Ph_3P–BH_3$ (1.917 Å)[21] and $Me_3P–BH_3$ (1.901 Å[22]), which may be associated with an O–H···H–B hydrogen–hydrogen bond to the neighbouring molecule leading to the formation of chains of molecules. Chains in the regions z = 0, 1/2, etc. are composed only of molecule 1 and those at z = 1/4, 3/4, etc. of molecule 2. Furthermore, adjacent molecules in the chains are related by *y*-axis translation, and thus each chain is formed from molecules of only one enantiomer. The average hydrogen–hydrogen bond length H···H is 1.90 Å (Table 1), which is significantly less than twice the van der Waals radius for hydrogen (2.4 Å) and lies at the lower end of the 1.7–2.2 Å range attributed to "dihydrogen bonds". The H–B bonds are slightly lengthened to 1.16 Å. The O–$H^{\delta+}$···$H^{\delta-}$ angles are very approximately linear (168, 150°), whereas the B–$H^{\delta-}$···$H^{\delta+}$ angles are both 119°.

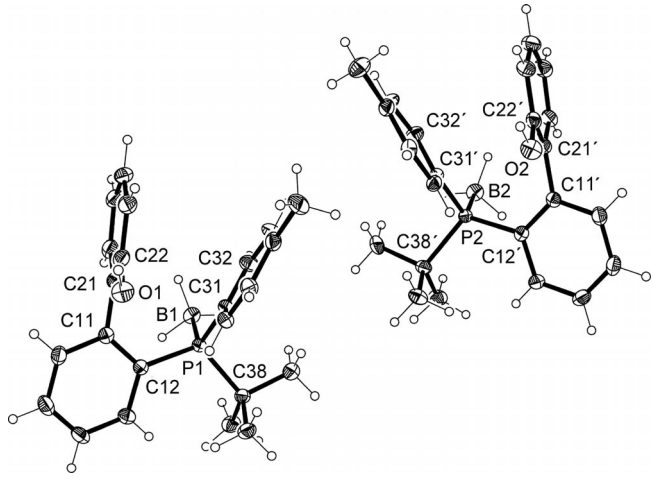


Figure 5. Molecular structures of the *R*,*R* (left) and *S*,*S* diastereoisomers (right) in the asymmetric unit of **6b**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P1–B1 1.938(2), P2–B2 1.931(2), P1–C31 1.8069(18), P1–C12 1.8325(18), P1–C38 1.8773, P2–C31′ 1.8073(18), P2–C12′ 1.8251(18), P2–C38′ 1.890(3); B1–P1–C12 111.52(9), B1–P1–C31 115.31(9), B1–P1–C38 108.98(9), C31–P1–C38 103.83(10).

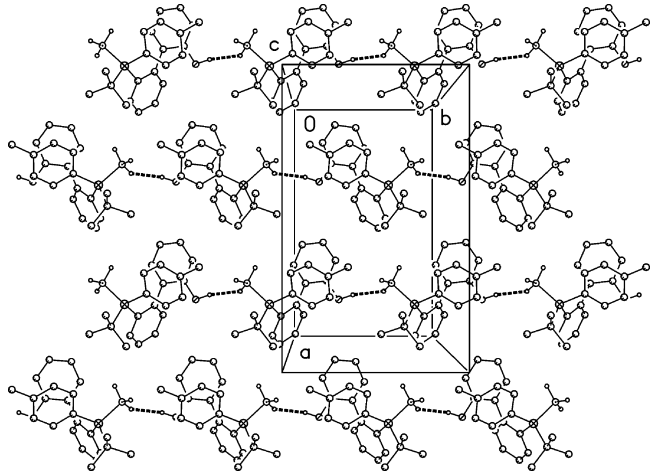


Figure 6. Unit cell of **6b**. The hydrogen–hydrogen bonds are indicated as thick dashed lines.

Table 1. Hydrogen–hydrogen bond lengths and angles in **6b**.[a]

Bond	Length [Å]	Bond	Angle [°]
O1–H1	0.92(2)	O1–H01–H1B_$1	168(3)
O2–H2	0.92(2)	O2–H02–H2B_$1	150(3)
H01–H1B_$1	1.93(3)	H01–H1B_$1–B1_$1	119(2)
H02–H2B_$1	1.88(3)	H02–H2B_$1–B2_$1	119(2)
B1–H1A, B1– H1C, B2–H2A, B2–H2C	1.09–1.11	C22–O1–H01	105(2)
B1–H1B, B2–H2B	1.17(2), 1.16(2)	C22′–O2–H02	105(2)

[a] Operator for generating equivalent atoms: $1: x, y – 1, z.

In the monoclinic crystals of the 2-hydroxybiphenylylphosphane–borane **6e** (Figure 7), with a higher donor strength and a lack of steric hindrance and asymmetry at the phosphorus atom, the P–B bond is somewhat shorter than in **6b**. The biphenyl interplanar angle is 80°. Hydrogen–hydrogen bonds (Table 2, Figures 7 and 8) are still formed but are three-centre O–H···H_2B interactions and therefore longer than in **6b**, which correspond to the longest values defined for two-centre "dihydrogen bonds". The bridging mode is reminiscent of bridging bonds in metal BH_4 complexes except that here the metal atom is replaced by the protic hydrogen atom. The OH bond in **6e** is 0.1 Å shorter than in **6b**, consistent with a weaker hydrogen–hydrogen bond. The molecules are connected through glide planes to form chains, vertical in Figure 8, parallel to (101).

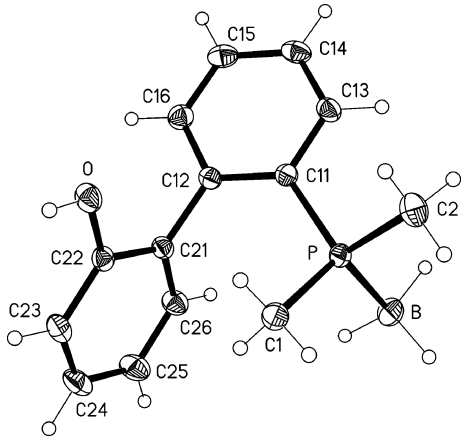
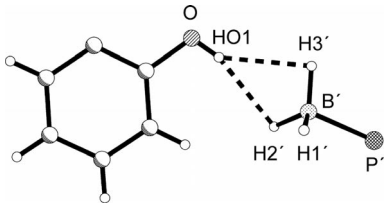


Figure 7. Molecular structure of **6e**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P–B 1.9165(13), P–C1 1.8045(11), P–C2 1.8133(12), P–C11 1.8222(10), C12–C21 1.4924(14), C11–C12 1.4087(14), C11–C13 1.4038(14), other C–C biphenyl bonds 1.3854–1.3994(14–18); B–P–C1 114.35(6), B–P–C2 111.56(6), B–P–C11 111.58(6), C(1)–P–C(2) 102.50(6), C(1)–P–C(11) 110.56(5), C(2)–P–C(11) 105.59(5).

Table 2. Hydrogen–hydrogen bond lengths and angles in **6e**.[a]



Bond	Length [Å]	Bond	Angle [°]
O–H01	0.81(2)	O–H01–H2_$1	161(2)
		O–H01–H3_$1	150(2)
H01–H2_$1	2.26(3)	H01–H2_$1–B_$1	90(1)
H01–H3_$1	2.24(3)	H01–H3_$1–B_$1	93(1)
B–H1	1.15(2)		
B–H2	1.16(2)		
B–H3	1.11(2)		

[a] Operator for generating equivalent atoms: $1: x + 1/2, $-y$ + 3/2, z + 1/2.

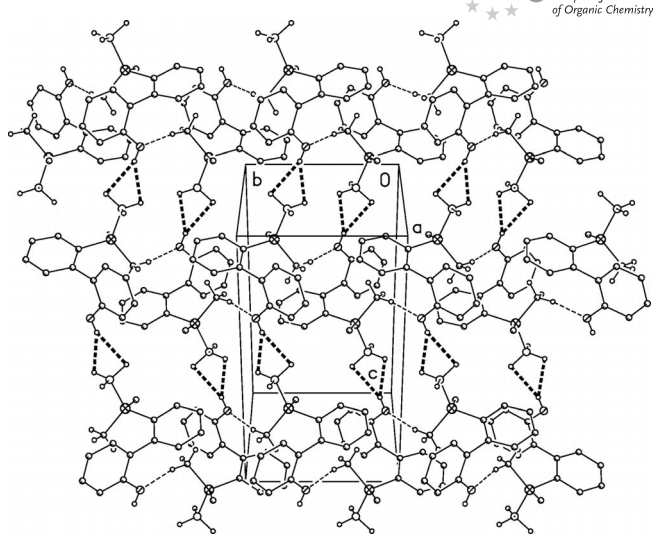


Figure 8. Unit cell of **6e**. The hydrogen–hydrogen bonds are indicated by thick dashed lines. View direction is perpendicular to (101).

For N–H functional amine–borane adducts, the influence of dihydrogen bonds on the crystal packing and reactivity in solution has been known for some years[20] and has stimulated extensive studies on the role of "dihydrogen bonds" in transition-metal hydride chemistry and catalysis and for use in hydrogen storage.[23] The structures of the 2-hydroxybiphenylylphosphanes **6b** and **6e**, in particular the relatively short H···H distance in the *P*-alkyl-*P*-aryl-hydroxybiphenylylphosphane **6b**, and the unexpectedly low reactivity of the hydroxy group of **6a** show that phosphane–boranes with acidic hydroxy groups are also able to form such hydrogen–hydrogen bonds.

Conclusions

Under defined conditions chlorodibenz[*c*,*e*][1,2]oxaphosphinine $\mathbf{1_{Cl}}$ reacted with bulky organolithium compounds R^1Li (R^1 = *t*Bu, mesityl) selectively with replacement of chlorine. Attempts at disubstitution with excess *t*BuLi failed in our hands under various conditions, whereas ring-opening metathesis with less bulky organolithium compounds R^2Li occurred easily. Reactions of $\mathbf{1_{Cl}}$ with 1 equiv. of R^2Li did not proceed selectively, being associated with a preference for P–O bond cleavage after replacement of chlorine by an organic substituent. With 2 equiv. of R^2Li, however, clean disubstitution was achieved. Workup by *O*-trimethylsilylation proved to be advantageous with various 2-hydroxyarylphosphanes because of the ambiphilic properties of these compounds. The trimethylsilyl group was easily removed with methanol in most cases, particularly if at least one *P*-alkyl group was present. The 2-hydroxybiphenylylphosphanes have low barriers to rotation around the C–C axis in contrast to *O*-acyl derivatives and are thus potential candidates for kinetic resolution by diastereoselective *O*-acylation with suitable chiral acid derivatives or for enantiomer separation by crystallization (cf. ref.[8]). Air-stable 2-

hydroxybiphenylylphosphane–borane adducts are expected to facilitate these operations but are unsuitable for this purpose as a result of a strongly diminished reactivity of the OH group towards *O*-acylation. Acylation must thus be performed before borane protection. The reason for this peculiar behaviour of 2-hydroxybiphenylylphosphane–boranes can be seen in terms of their unusual structures. Crystal structure analyses revealed that the 2-hydroxybiphenylylphosphane–boranes are new examples of compounds with an unconventional "dihydrogen bond" between a protic and a hydridic hydrogen atom, polar enough to display this short H···H distance but not enough to decompose at ordinary temperature with the evolution of dihydrogen. At a higher temperature, however, the compounds decompose with the formation of B–O bonds, which can easily by cleaved by alcohols, providing a route for the deprotection of the ligands.

Experimental Section

General: All reactions were carried out under argon by using standard Schlenk techniques. Solvents were dried and freshly distilled before use. Me_3SiCl was recondensed in vacuo. 6-Chloro-6*H*-dibenz[*c*,*e*][1,2]oxaphosphinine (**1$_{Cl}$**) was synthesized according to a literature procedure.[24] Other chemicals were purchased. NMR spectroscopic data were recorded with a Bruker multinuclear FT-NMR ARX 300 spectrometer at 300.1 (^{1}H), 75.5 (^{13}C) and 121.5 MHz (^{31}P) or a Bruker Avance 600 spectrometer at 600.1 (^{1}H) and 150 MHz (^{13}C). Chemical shifts are given as δ values with reference to TMS and H_3PO_4 (85%). Coupling constants of the ^{1}H NMR spectra refer to J_{HH} and those of ^{13}C NMR spectra to J_{PC} unless indicated otherwise. Doublets of doublets, which by similar coupling constants appear as distorted triplet, are indicated as t with two similar *J* values. Further doublet or multiple fine splitting is indicated by td or tm. Assignments of the biphenyl ring atoms are as indicated in Scheme 1 with those of the *P*-phenyl ring denoted by primes. For dibenzoxaphosphinines the same assignment numbers are used. External phenyl groups are indicated by *i*, *o*, *m* and *p* or, if substituted, by 1′′ etc. Assignments are based on 2D experiments (C–H and H–H COSY) of selected compounds and are supported by DEPT-135 analyses, for other compounds they are tentative. Mass spectra (EI, 70 eV) were recorded with an Intectra AMD40 single-focusing sector field mass spectrometer and HRMS spectra with a MAT95 (EI, 70 eV) spectrometer. Elemental analyses were determined by using a LECO CHNS-932 analyser under standard conditions. A Sanyo Gallenkamp melting-point apparatus was used to determine melting points, for air-sensitive substances in a closed capillary under nitrogen.

6-*tert*-Butyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphinine (1$_{tBu}$): A solution of *t*BuLi in pentane (12.7 mL, 1.5 M, 19.0 mmol) was added dropwise to a solution of **1$_{Cl}$** (4.46 g, 19.0 mmol) in toluene (30 mL) at –30 °C, which led to formation of a precipitate. (Fast addition and higher temperatures gave product mixtures.) After the addition was complete, the reaction mixture was warmed to room temperature and stirred overnight. Then the precipitate was separated, and the filtrate was removed in vacuo. The residue was distilled at 130–140 °C/10^{-2} mbar in a distillation apparatus with an air-cooled condensation tube, diameter 10 mm. Colourless crystals deposited in this tube, yield 3.1 g (64%), m.p. 88–90 °C. ^{1}H NMR ($CDCl_3$): δ = 0.88 (d, $^3J_{PH}$ = 13.0 Hz, 9 H, CMe_3), 7.04 (br. d, ^3J = 8, ^4J = 1.2 Hz, 1 H, 3-H), 7.07 (td, $^3J \approx {}^3J_{PH}$ = 7–8, ^4J = 1.5 Hz, 1 H, 3′-H), 7.25 (td, ^3J = 7.7, ^4J = 1.6 Hz, 1 H, 5-H), 7.32–7.42 (m, 2 H, 4-H, 4′-H), 7.49 (m, 1 H, 5′-H), 7.79 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, 6′-H), 7.89 (br. d, ^3J = 8 Hz, 1 H, 6-H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 106.4 ppm. MS (EI, 70 eV, 120 °C): *m*/*z* (%) = 257 (4), 256 (23) $[M]^+$, 200 (45), 199 (100), 151 (20), 57 (4). $C_{16}H_{17}OP$ (256.28): calcd. C 74.99, H 6.69; found C 75.25, H 6.37.

Hydrolysis and Air Oxidation of 1$_{tBu}$ to 3 and 4: Treatment of **1$_{tBu}$** in $CDCl_3$ with water led to **3**, which, as a result of hindered rotation at 25 °C, forms a major and minor diastereoisomer (ca. 75:25). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 43.8 (major), 58.9 (minor) ppm; intensity ratio ca. 4:1; proton coupling led to doublets ($^1J_{PH} \approx$ 487 Hz) with further splitting ("quint", $^3J \approx$ 16 Hz). ^{1}H NMR ($CDCl_3$): δ = 0.91 (d, $^3J_{PH}$ = 17.1 Hz, 1/4 × 9 H, CMe_3), 0.94 (d, $^3J_{PH}$ = 16.5 Hz, 3/4 × 9 H, CMe_3), 6.93 (d, $^1J_{PH}$ = 488 Hz, 3/4 H, HP=O), 7.00 (d, $^1J_{PH}$ = 465 Hz, 1/4 H, HP=O), 6.86 (td, ^3J = 7.4, ^4J = 1.2 Hz, 5-H_{ma}), 7.01 (td, 5-H_{mi}), 7.06–7.16 (td and dd, 2 $H_{ma/mi}$), 7.19–7.3 (m, 2 H), 7.35–7.50 (m, 1 H), 7.54–7.68 (m, 1 H), 7.91 (ddd, $^3J_{PH}$ = 10.8, ^3J = 7.7, ^4J = 1.2 Hz, 1 H, 3′-H_{ma}) ppm. From a concentrated solution of **1$_{tBu}$** in moist C_6D_6 single crystals of **3** deposited in the NMR tube. Crystal data are compiled in Table 3. Selected bond lengths and angles are presented in Figure 3. Slow diffusion of air into a plastic-capped NMR sample for 6 d led to complete air oxidation and the formation of **4**: ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 45.3 ppm; the proton-coupled multiplet appears as a "sept" ($^3J_{PH}$ = 16 Hz) with fine splitting. ^{1}H NMR ($CDCl_3$): δ = 1.54 (d, $^3J_{PH}$ = 16.5 Hz, CMe_3), 7.15–7.23 (dt, 2 H), 7.25–7.40 (m, 1 H), 7.45–7.60 (tm, 1 H), 7.65–7.75 (tm, 1 H), 7.85–8.05 (m, 3 H) ppm.

6-Mesityl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphinine (1$_{Mes}$): A solution of *t*BuLi (16.0 mL, 1.5 M, 23.9 mmol) in pentane was added at –30 °C to a solution of bromomesitylene (3.60 mL, 23.9 mmol) in tetrahydrofuran (15 mL). After stirring at room temperature for 2 h, the resulting mesityllithium was added in small portions at –30 °C to a solution of **1$_{Cl}$** (5.1 g, 21.7 mmol) in toluene (35 mL). A yellow mixture was formed, which was stirred at room temperature overnight. Because NMR monitoring indicated incomplete conversion of **1$_{Cl}$**, a second portion of mesityllithium was prepared and added at –30 °C. After stirring at room temperature for 1 d, excess chlorotrimethylsilane (10 mL, 80 mmol) was added (ca. 0 °C) to trap unconverted organolithium reagent. The mixture was allowed to react at 20 °C for 2 h, and then the precipitate was filtered off and washed with diethyl ether. The solvent was removed in vacuo to yield the crude product as a yellow viscous liquid. High-vacuum distillation at 160–170 °C/10^{-5} mbar gave 3.64 g (53%) of **1$_{Mes}$** as white solid (m.p. 82–85 °C). ^{1}H NMR, H–H COSY ($CDCl_3$): δ = 2.26 (s, 3 H, 4′′-Me), 2.36 (2 s, 6 H, 2′′,6′′-Me), 6.84 (dd, *J* = 2.5, 0.7 Hz, 2 H, 3′′-H), 6.97 (br. d, ^3J = 7.6 Hz, 1 H, 3-H), superimposed 6.98 (tdd, $^3J \approx {}^3J_{PH}$ = 7–8, ^4J = 1.4, ^5J = 0.5 Hz, 1 H, 3′-H), 7.06 (td, ^3J = 7.8, 7.4, ^4J = 1.3 Hz, 1 H, 5-H), 7.19 (td, ^3J = 8, 7.3, ^4J = 1.7 Hz, 1 H, 4-H), 7.20 (tt, ^3J = 7.5, 7.4, ^4J = 1, $^5J_{PH}$ = 0.7 Hz, 1 H, 4′-H), 7.36 (td, ^3J = 7.6, 7.5, ^4J = 1, $^5J_{PH}$ = 0.5 Hz, 1 H, 5′-H), 7.69 (dt, ^3J = 7.5, ^4J = 1.3, *J* = 1.2 Hz, 1 H, 6′-H), 7.72 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR, C–H COSY ($CDCl_3$): δ = 21.13, 22.15, 22.39 (Me), 120.55 (d, ^3J = 2.6 Hz, C-3), 123.05 (C-5), 123.32 (d, ^3J = 1.6 Hz, C-6′), 125.05 (br., C-6), 125.25 (d, ^3J = 8.1 Hz, C_q-1), 127.90 (d, ^2J = 23.8 Hz, C-3′), 127.98 (d, ^3J = 5.3 Hz, C-4′), 129.54 (br., C-5′), 129.76 (C-4), 130.19 (d, ^3J = 2.7 Hz, 2 C-3′′), 131.75 (d, ^1J = 33.3 Hz, C_q-2′), 134.57 (d, ^3J = 9.4 Hz, C_q-1′′), 135.91 (d, ^2J = 22.6 Hz, C_q-1′), 141.17 (C_q-4′′), 144.32 (d, ^2J = 18.6 Hz, 2 C_q-2′′), 152.37 (d, ^4J = 2.6 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 110.5 ppm. MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 319 (19), 318 (100) $[M]^+$, 317 (93), 316 (16), 216 (38), 199 (57), 151 (36), 119 (49), 91 (20), 77 (11), 41

(20). $C_{21}H_{19}OP$ (318.35): calcd. C 79.23, H 6.02; found C 79.06, H 6.09.

2′-[*tert*-Butyl(methyl)phosphanyl]-2-(trimethylsilyloxy)-1,1′-biphenyl (2a): A solution of methyllithium in diethyl ether (8.1 mL, 1.6 M, 13.0 mmol) was added dropwise at –80 °C to a solution of compound $\mathbf{1}_{tBu}$ (3.015 g, 11.8 mmol) in THF (35 mL). The mixture was warmed to room temperature and stirred overnight to complete the conversion. Then chlorotrimethylsilane (1.65 mL, 13 mmol) was added dropwise. After stirring for 5 h, the precipitate was separated by filtration, the solvent removed from the filtrate, and the residue distilled at 100–120 °C/9×10^{-6} mbar to give 2.28 g (56%) of a colourless viscous liquid. ^{1}H NMR, H–H COSY ($CDCl_3$, ref. solv.): δ = –1.32 (s, 9 H, $SiMe_3$), 0.90 (d, ^3J = 11.8 Hz, 9 H, CMe_3), 1.38 (d, ^2J = 5.4 Hz, 3 H, PMe), 6.99 (br. d, ^3J = 8.0 Hz, 1 H, 3-H), 7.09 (br. t, ^3J = 7.3 Hz, 1 H, 5-H), 7.23–7.31 (m, 2 H, 6′-H, 6-H), 7.33 (td, ^3J = 8.0, 7.3, ^4J = 1.6 Hz, 1 H, 4-H), 7.43 (td, $^3J \approx 7$, ^4J = 1.7 Hz, 1 H, 5′-H), 7.44 (td, $^3J \approx 7$, ^4J = 1–2 Hz, 1 H, 4′-H), 7.63 (ddd, $^3J_{PH}$ = 3.8, $^3J \approx 7$, ^4J = 1.7 Hz, 1 H, 3′-H) ppm. ^{13}C{^{1}H} NMR, C–H COSY ($CDCl_3$): δ = 0.07 ($SiMe_3$), 6.23 (d, ^1J = 21.2 Hz, PMe), 27.06 (d, ^2J = 14.5 Hz, C*Me*$_3$), 29.42 (d, ^1J = 12.6 Hz, *C*Me_3), 119.91 (C-3), 121.10 (C-5), 126.16 (C-5′), 128.33 (C-4), 128.37 (C-4′), 130.53 (d, ^3J = 5.6 Hz, C-6′), 131.26 (d, ^2J = 3.6 Hz, C-3′), 131.43 (C-6), 135.20 (d, ^3J = 5.6 Hz, C_q-1), 137.07 (d, ^1J = 20.3 Hz, C_q-2′), 146.21 (d, ^2J = 33.3 Hz, C_q-1′), 151.82 (C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –20.5, –25.1 ppm; rel. intensity 93:7. MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 344 (3) $[M]^+$, 328 (7), 309 (17), 287 (14), 256 (20), 255 (100), 252 (27), 199 (84), 195 (44), 183 (28), 181 (29), 57 (26). $C_{20}H_{29}OPSi$ (344.50): calcd. C 69.73, H 8.48; found C 70.14, H 8.46.

2′-[*tert*-Butyl(*p*-tolyl)phosphanyl]-2-(trimethylsilyloxy)-1,1′-biphenyl (2b): A solution of *p*-tolyllithium was prepared by dropwise addition of *t*BuLi solution (12.7 mL, 1.5 M in pentane, 19.0 mmol) at –70 °C to *p*-bromotoluene (3.25 g, 19.0 mmol) dissolved in diethyl ether (20 mL) and stirring at room temperature for 3 h. The resulting solution was added at –90 °C to a solution of $\mathbf{1}_{tBu}$ (4.4 g, 17.2 mmol) in THF. The mixture was warmed to room temperature and stirred overnight. Then chlorotrimethylsilane (2.55 mL, 20 mmol) was added dropwise. After stirring for 5 h, the precipitate was filtered off and the solvent removed in vacuo. The crude product was purified by high-vacuum distillation at 160–180 °C/10^{-6} mbar to give 4.16 g (57%) of a colourless viscous liquid. The diastereoisomer ratio A/B was ca. 60:40 (by *t*Bu ^{1}H NMR integration). ^{1}H NMR, H–H COSY ($CDCl_3$, ref. solv.): δ = –0.08, 0.09 (2 s, 60:40, 9 H, $SiMe_{3AB}$), 1.02 (d, ^3J = 12.2 Hz, 5.4 H, CMe_{3A}), 1.10 (d, ^3J = 12.4 Hz, 3.6 H, CMe_{3B}), 2.34 (br. s, 3 H, *p*-Me), 6.61 (br. d, ^3J = 7.2 Hz, 0.4 H, 6-H_B), 6.70 (br. t, ^3J = 7.5, 7.3 Hz, 0.4 H, 5-H_B), 6.84, 6.85 (2 d, ^3J = 7.8 Hz, 1 H, 3-H_{AB}), 7.02 (superimposed t, 5-H_A), 7.02–7.12 (m, 2 *m*-H_B, 2 *o*-H_A), 7.13–7.30 (m, 4-H_B, 2 *o*-H_B, 6′-H_A, 4-H_A, 6-H_A, 6′-H_B), 7.27–7.42 (m, 5′-H_A, 4′-H_B, 5′-H_B, 4′-H_A), 7.44–7.50 (br. t, 2 *o*-H_A), 7.58 (br. d, ^3J = 6.9 Hz, 0.6 H, 3′-H_A), 7.85 (br. m, 0.4 H, 3′-H_B) ppm. ^{13}C{^{1}H} NMR, C–H COSY, DEPT ($CDCl_3$): δ = 0.27 ($SiMe_{3A}$), 0.47 ($SiMe_{3B}$), 21.15 (br., *p*-Me), 28.83 (d, ^2J = 15.1 Hz, C*Me*$_{3A}$), 28.89 (d, ^2J = 15.7 Hz, C*Me*$_{3B}$), 30.52 (d, ^1J = 17.3 Hz, *C*Me_{3B}), 31.48 (d, ^1J = 16.8 Hz, *C*Me_{3A}), 119.05 (C-3$_B$), 119.63 (C-3$_A$), 120.06 (C-5$_B$), 120.75 (C-5$_A$), 126.23 (C-5′$_B$), 126.27 (C-5′$_A$), 127.48 (C-4′$_B$), 128.14 (C-4$_B$), 128.26–128.38 (m, 2 *m*-CH_{AB}, C-4$_A$, C-4′$_A$), 130.51 (d, ^3J = 6.8 Hz, C-6′$_A$), 131.5 (superimposed, C-6′$_B$), 131.57 (superimposed, C-6$_A$), 132.40 (d, ^3J = 4.6 Hz, C-6$_B$), 133.40 (superimposed d, ^2J = 17.7 Hz, 2 *o*-CH_A, C-3′B), 133.58 (superimposed d, $^3J \approx 9$ Hz, C_q-1$_B$), 134.17 (d, ^2J = 19.2 Hz, 2 *o*-CH_B), 134.92 (d, ^2J = 3.2 Hz, C-3′$_A$), 135.12 (superimposed d, $^1J \approx 19$ Hz, C_q-*i*$_B$), 135.20 (superimposed br. d, $^4J \approx 7$ Hz, C_q-1$_A$), 135.12 (d, ^1J = 21.6 Hz, C_q-i$_A$), 136.61 (d, ^1J = 20.9 Hz, C_q-2′), 136.67, 137.33 (C_q-p_{AB}), 137.47 (d, ^1J = 20.5 Hz, C_q-2′), 146.21 (d, ^2J = 30.6 Hz, C_q-1′$_B$), 146.92 (d, ^2J = 34.3 Hz, C_q-1′$_A$), 152.04 (C_q-2$_B$), 152.37 (C_q-2$_A$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 6.7, 5.5 ppm (A/B ca. 60:40). MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 421 (3), 420 (2) $[M]^+$, 363 (16), 332 (14), 331 (66), 309 (31), 308 (37), 275 (41), 252 (70), 251 (28), 199 (35), 195 (100), 181 (73), 106 (41), 74 (48). $C_{26}H_{33}OPSi$ (420.20): calcd. C 74.25, H 7.91; found C 73.98, H 8.15.

2′-[Mesityl(methyl)phosphanyl]-2-(trimethylsilyloxy)-1,1′-biphenyl (2c): A solution of MeLi in diethyl ether (7.8 mL, 1.6 M, 12.5 mmol) was added to a solution of $\mathbf{1}_{Mes}$ (3.59 g, 11.3 mmol) in THF (35 mL) cooled to –90 °C. The reaction mixture was warmed to room temperature. After stirring at room temperature overnight, chlorotrimethylsilane (3.3 mL, 26 mmol) was added. The reaction mixture was stirred for 5 h, the precipitate was filtered off, the solvent removed in vacuo, and the product distilled at 160–170 °C/1.2×10^{-5} mbar to yield 3.07 g (67%) as a colourless viscous liquid. ^{1}H NMR ($CDCl_3$): δ = 0.04, 0.07 (2 s, 9 H, $SiMe_3$), 1.42 (d, ^2J = 5.1 Hz, 1.5 H, PMe), 1.49 (d, ^2J = 5.7 Hz, 1.5 H, PMe), 2.04, 2.08 (2 s, 6 H, 2′′,6′′-Me), 2.19, 2.23 (2 s, 3 H, 4′′-Me), 6.45 (d, ^3J = 8.1 Hz, 0.5 H, 3-H), 6.61 (v br. s, 2 H, 3′′-H), 6.71 (v br. s, 1 H), 6.80 (d, ^3J = 8 Hz, 0.5 H, 3-H), 6.90 (t, ^3J = 7.7, 7.3 Hz, 0.5 H, 5-H), 7.00–7.15 (m, 2 H, aryl), 7.21–7.38 (m, 3 H, aryl), ca. 7.10 (m, 0.5 H, aryl) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –38.2, –39.4 ppm (A/B ca. 1:1). MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 407 (13), 406 (42) $[M]^+$, 405 (26), 318 (25), 317 (100), 213 (8), 199 (13). $C_{25}H_{31}OPSi$ (406.57): calcd. C 73.85, H 7.69; found C 73.66, H 7.80.

Hydrolysis and Air Oxidation of 2c to $\mathbf{5c_{ox}}$: Attempts at crystallization of **2c** in various solvents by layering with hexane failed under inert conditions, whereas crystals of $\mathbf{5c_{ox}}$ were formed from a sample allowed to stand in an open beaker with contact to air and moisture. Crystal data are compiled in Table 3. Selected bond lengths and angles are displayed in Figure 4.

Detection of 2′-[*tert*-Butyl(mesityl)phosphanyl]-2-(trimethylsilyloxy)-1,1′-biphenyl (2d): A solution of *t*BuLi in pentane (2.7 mL, 1.5 M, 4.05 mmol) was added dropwise to a solution of $\mathbf{1}_{Mes}$ (1.138 g, 3.58 mmol) in THF (10 mL) cooled to –100 °C. Residual *t*BuLi in the dropping funnel was rinsed with *n*-hexane (10 mL) and added to the reaction mixture, which then was warmed to room temperature. The colour changed from pale-brown after the addition to red at –70 °C. After stirring at room temperature overnight, NMR monitoring showed a broad ^{31}P signal for the ring-cleavage product and a small sharp signal for unreacted $\mathbf{1}_{Mes}$, conversion >95%. Excess $ClSiMe_3$ (2.0 mL, 15.7 mmol) was added and the mixture stirred overnight. The colour turned slowly to pale-yellow. Then the precipitate was filtered off, the solvent removed in vacuo, and the product distilled at 180–200 °C/10^{-5} mbar to yield 0.68 g (40%) of a colourless viscous liquid. ^{1}H NMR ($CDCl_3$): δ = 0.04, 0.07 (2 s, 9 H, $SiMe_3$), 1.315 (d, ^3J = 12.6 Hz, 4.5 H, $PCMe_3$), 1.32 (d, ^3J = 12.9 Hz, 4.5 H, $PCMe_3$), 1.90, 1.93 (2 br. s, 6 H, 2′′,6′′-Me), 2.15, 2.21 (2 s, 3 H, 4′′-Me), 6.02 (dd, ^3J = 7.4, ^4J = 1.7 Hz, 0.5 H, 3-H), 6.30 (dd, ^3J = 8, ^4J = 1 Hz, 0.5 H, 3-H), 6.30 (superimposed td, ^3J = 7–8, ^4J = 1 Hz, 0.5 H, 5-H), 6.53 (br. s, 1 H, 3′′-H), 6.63 (br. s, 1 H, 3′′-H), 6.74, 6.86 (2 d, ^3J = 7–8 Hz, 6-H) superimposed by 6.70–7.10 (m, 4-H, 3′-H or 6′H), 7.15–7.40 (m, 4′-H, 5′-H), 7.93 (br. d, ^3J = 7.4 Hz, 1 H, 6′-H or 3′H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –1.4, –2.9 ppm (A:B ca. 1:1).

2′-(Dimethylphosphanyl)-2-(trimethylsilyloxy)-1,1′-biphenyl (2e): A solution of MeLi in diethyl ether (24 mmol, 15 mL, 1.6 M) was added dropwise to a solution of compound $\mathbf{1}_{Cl}$ (2.57 g, 11.0 mmol) in diethyl ether/THF (10:7 mL) at –90 °C. The mixture was warmed

to room temperature, stirred overnight, and chlorotrimethylsilane (22 mmol, 2.8 mL) was added slowly. After stirring for 4 h, the precipitate was separated by filtration, the solvent removed from the filtrate, and the residue distilled at around 90 °C/10^{-4} mbar to give 1.28 g (39%) of a colourless viscous liquid **2e**. ^{1}H NMR ($CDCl_3$): δ = 0.06 (s, 9 H, $SiMe_3$), 1.19 (br. s, 3 H, PMe_A), 1.28 (br. s, 3 H, PMe_B), 6.96 (br. dd, ^3J = 8.0, ^4J = 1.1 Hz, 1 H, 3-H), 7.08 (td, ^3J = 7.4, ^4J = 1.2 Hz, 1 H, 5-H), 7.30 (superimposed dd, $^3J \approx 7.2$, ^4J = 1.6 Hz, 1 H, 6-H), 7.24–7.30 (m, 1 H, 6′-H), 7.32 (td, ^3J = 8.0, 7.4, ^4J = 1.8 Hz, 1 H, 4-H), 7.39 (td, $^3J \approx 7.5$, ^4J = 1.6 Hz, 1 H, 5′-H or 4′-H), 7.43 (m, $^3J \approx 7.4$, ^4J = 1.7 Hz, 1 H, 4′-H or 5′-H), 7.63 (ddd, $^3J_{PH}$ = 3.8, ^3J = 6.9, ^4J = 1.7 Hz, 1 H, 3′-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 0.20 ($SiMe_3$), 14.05 (d, ^1J = 14.1 Hz, PMe), 15.15 (d, ^1J = 13.8 Hz, PMe), 119.70 (C-3), 120.94 (C-5), 127.16, 127.60 (br.), 128.57, 128.77 (br. C-4, C-4′, C-6, C-5′), 130.24 (d, ^2J = 5.3 Hz, C-6′), 131.19 (d, ^3J = 2.6 Hz, C-3′), 133.91 (d, ^3J = 5.6 Hz, C_q-1), 141.11 (d, ^1J = 15.1 Hz, C_q-2′), 144.40 (d, ^2J = 29.3 Hz, C_q-1′), 152.45 (C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –53.6 ppm. HRMS (EI): calcd. for $C_{17}H_{23}OPSi^+$ (302.1250); found 302.1253.

2′-(Di-*o*-anisylphosphanyl)-2-(trimethylsilyloxy)-1,1′-biphenyl (2f): A solution of *t*BuLi (20 mL, 1.5 M in pentane, 30.0 mmol) was added at –78 °C to a solution of *o*-bromoanisole (3.72 mL, 30.0 mmol) in diethyl ether (25 mL). After stirring for 2 h at room temperature the solution of *o*-anisyllithium was added dropwise at –90 °C to a solution of $\mathbf{1_{Cl}}$ (3.187 g, 13.6 mmol) in THF (35 mL). The reaction mixture was warmed to room temperature and stirred overnight. Then $ClSiMe_3$ (4.0 mL, 31.5 mmol) was added, and, after stirring at 20 °C for 2 h and filtration, the solvent was removed in vacuo. The crude product was purified by crystallization from diethyl ether/hexane (3:1) to afford 6.28 g (95%) of colourless crystals, m.p. 121–123 °C. ^{1}H NMR ($CDCl_3$): δ = 0.02 (s, 9 H, $SiMe_3$), 3.62 (s, 6 H, 2′′-OMe), 6.73 (ddd, ^3J = 7.6, $^3J_{PH}$ = 4.3, ^4J = 1.8 Hz, 2 H, 3′′-H), 6.76–6.86 (br. m, 6 H, 5′′-H, 3-H, 5-H, 6′′-H), 6.99–7.04 (vbr. d, 1 H, 6-H), 7.03 (ddd, ^3J = 7.7, $^3J_{PH}$ = 3.8, ^4J = 1.1 Hz, 1 H, 3′-H), 7.12 (td, ^3J = 7–8 Hz, ^4J = 1.8 Hz, 1 H, 4-H), 7.19 (td, ^3J = 7.5, 7.1, ^4J = 1.7 Hz, 1 H, 4′-H or 5′-H), 7.24–7.31 (m, 3 H, 2 4′′-H, 6′-H), 7.33 (td, ^3J = 7.5, 7.3, ^4J = 1.3 Hz, 1 H, 5′-H or 4′-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 0.36 ($SiMe_3$), 55.48 (br., OMe), 110.0 (vbr., 2 C-3′′), 119.25, 120.30 (C-3, C-5), 120.69 (st, 2 C-5′′), 126.82, 127.70, 128.28 (C-4′, C-4, C-5′), 129.71 (st, 2 C-4′′), 130.76 (d, ^3J = 5.6 Hz, C-6′ or C-3′), 131.87 (d, ^2J = 4.6 Hz, C-3′ or C-6′), 133.16 (d, ^1J = 6.8 Hz, C_q-2′), 133.96 (C-6), 134.29 (st br., 2 C-6′′), 145.01 (d, ^2J = 31.9 Hz, C_q-1′), 152.57 (C_q-2), 161.29 (d, ^2J = 16.2 Hz, 2 C_q-2′′) ppm; C_q-1 and C_q-1′′ signals superimposed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –33.7 (br.) ppm. MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 487 (18), 486 (100) $[M]^+$, 398 (27), 397 (94), 351 (4), 108 (4), 74 (12). HRMS (EI): calcd. for $C_{29}H_{31}O_3PSi^+$ 486.1780; found 486.1778.

2′-[*tert*-Butyl(methyl)phosphanyl]-2-hydroxy-1,1′-biphenyl (5a): A solution of **2a** (4.594 g, 13.3 mmol) in methanol (15 mL) was heated at reflux for 7 h. Removal of the solvent and $MeOSiMe_3$ in vacuo gave 3.60 g (100%) of colourless crystals, m.p. 93–94 °C, with a diastereoisomer ratio A/B of ca. 80:20 based on ^{1}H NMR integration of Me signals. ^{1}H NMR ($CDCl_3$): δ = 0.81, 0.815 (2 d, $^3J_{PH}$ = 12.4 Hz, 9 H, CMe_3), 1.26 (d, $^2J_{PH}$ = 5.3 Hz, 0.75 H, PMe_B), 1.35 (d, $^2J_{PH}$ = 4.2 Hz, 2.25 H, PMe_A), 5.6 (br. s, 1 H, OH), 6.98 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1 H, 5-H), 7.00 [d, $^3J \approx 8$ Hz (sh), 1 H, 3-H], 7.14 (dd, ^3J = 7.5, ^4J = 1.4 Hz, 1 H, 6-H), 7.23–7.35, 7.39–7.48 (2 m, 4 H, 4,4′,5′,6′-H), 7.54 (m, ΣJ = 12.3 Hz, 0.8 H, 3′-H_A), 7.62–7.7 (m, 0.2 H, 3′-H_B) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –19.3, –24.7 ppm (A/B ≈ 80:20). For analytical characterization as the borane adduct, see below.

Air Oxidation: An ethereal solution of **5a** was stirred with air contact for about 12 h. NMR measurement showed oxidation to the corresponding phosphane oxide. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 53.1, 57.6 ppm (20:80). ^{1}H NMR ($CDCl_3$): δ = 0.94 (d, $^3J_{PH}$ = 15.4 Hz, CMe_{3ma}), 1.08 (d, $^3J_{PH}$ = 14.9 Hz, CMe_{3mi}), 1.84 (d, $^2J_{PH}$ = 14.7 Hz, Me_{mi}), 1.85 (d, $^2J_{PH}$ = 12.0 Hz, Me_{ma}), 6.80–7.60 (8 H, aryl) ppm.

2′-[*tert*-Butyl(methyl)phosphanyl]-2-hydroxy-1,1′-biphenyl–Borane (6a): Reaction of excess $H_3B{\cdot}SMe_2$ in dichloromethane (6.1 mL, 1 M, 6.1 mmol) with **5a** (1.64 g, 6.02 mmol) in CH_2Cl_2 (20 mL) at –80 to 20 °C (4 h), removal of the solvent in vacuo, and crystallization from methanol furnished 1.69 g (98%) of colourless crystals, m.p. 141–144 °C (decomposition), with a diastereoisomer ratio A/B of ca. 75:25 (based on ^{1}H NMR integration). ^{1}H NMR ($CDCl_3$): δ = 0.1–1.2 (v. br., 3 H, BH_3), 1.02 (superimposed d, $^2J_{PH} \approx 11$ Hz, 2.3 H, PMe_A), 1.06 (d, $^3J_{PH}$ = 13.8 Hz, 9 H, CMe_{3AB}), 1.15 (d, $^2J_{PH}$ = 9.9 Hz, 0.7 H, PMe_B), 4.69 (s, 1 H, OH), 6.916 (dd, ^3J = 8.1, ^4J = 1 Hz, 3-H_A), 6.92 (dd, ^3J = 8.1, ^4J = 1 Hz, 3-H_B), 6.96 (td, ^3J = 7.5, ^4J = 1.2 Hz, 5-H_B), 6.97 (td, ^3J = 7.5, ^4J = 1.2 Hz, 5-H_A), 7.07 (dd, ^3J = 7.5, ^4J = 1.8 Hz, 0.25 H, 6-H_B), 7.15 (dd, ^3J = 7.5, ^4J = 1.8 Hz, 0.75 H, 6-H_A), 7.22–7.27 (m, 1 H, 6′-H_{AB}), 7.31 (td, ^3J = 8.1, 7.4, ^4J = 1.7 Hz, 1 H, 4-H_B), 7.32 (td, ^3J = 8.1, 7.4, ^4J = 1.7 Hz, 1 H, 4-H_A), 7.49–7.61 (m, 2 H, 4′-H_{AB}, 5′-H_{AB}), 8.07 (ddt, $^3J_{PH}$ = 12.7, ^3J = 7.1, $^4J \approx {}^5J$ = 1.0–1.5 Hz, 0.25 H, 3′-H_B), 8.16 (ddt, $^3J_{PH}$ = 12.7, ^3J = 7.1, $^4J \approx {}^5J$ = 1.0–1.5 Hz, 0.75 H, 3′-H_A) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 33.8 (pseudo-d), ca. 32 (shoulder) ppm. MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 286 (7) $[M]^+$, 256 (8), 255 (52), 215 (8), 199 (38), 118 (15), 93 (100), 67 (28). $C_{17}H_{24}BOP$ (286.16): calcd. C 71.35, H 8.45; found C 71.02, H 8.70.

2′-[*tert*-Butyl(*p*-tolyl)phosphanyl]-2-hydroxy-1,1′-biphenyl (5b): A solution of **2b** (2.11 g, 5.02 mmol) in methanol (10 mL) was heated at reflux for 7 h. The solvent and Me_3SiOMe were removed in vacuo to yield 1.74 g (100%) of colourless crystals, m.p. 127–133 °C, with a diastereoisomer ratio A/B of ca. 50:50. ^{1}H NMR ($CDCl_3$): δ = 1.08 (d, ^3J = 12.8 Hz, 4.5 H, CMe_3), 1.17 (d, ^3J = 12.7 Hz, 4.5 H, CMe_3), 2.30, 2.33 (2 s, 3 H, *p*-Me), 4.88 (br., 0.5 H, OH), 5.18 (br., 0.5 H, OH), 6.41 (br. d, ^3J = 7.4 Hz, 0.5 H, 3-H), 6.59 (br. t, ^3J = 7.3 Hz, 0.5 H, 5-H), 6.84 (br. d, ^3J = 7.5 Hz, 0.5 H, 3-H), 6.90–7.30 (m, 6.5 H), 7.30–7.52 (m, 3 H), 7.68 (ddd, ^3J = 7.3, $^3J_{PH}$ = 3.8, ^4J = 1.1 Hz, 0.5 H, 3′-H), 7.92 (m, 0.5 H, 3′-H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 6.87, 7.01 ppm (A/B ≈ 50:50). MS (EI, 70 eV, 345 °C): *m*/*z* (%) = 348 (9) $[M]^+$, 332 (22), 331 (100), 291 (15), 283 (14), 275 (56), 272 (11), 199 (63), 183 (16), 182 (10), 151 (11), 74 (17). HRMS (EI): calcd. for $C_{23}H_{25}OP^+$ 348.1643; found 348.1645.

2′-[*tert*-Butyl(*p*-tolyl)phosphanyl]-2-hydroxy-1,1′-biphenyl–Borane (6b): Reaction of excess $H_3B{\cdot}SMe_2$ in dichloromethane (0.52 mL, 1 M, 0.52 mmol) with **5b** (178 mg, 0.51 mmol) in CH_2Cl_2 (5 mL) at –80 to 20 °C (4 h), removal of the solvent in vacuo, and crystallization from methanol furnished 175 mg (95%) of colourless crystals, m.p. 135–139 °C (decomposition), with a diastereoisomer ratio A/B of ca. 56:44 (based on ^{1}H NMR integration). Single crystals studied by X-ray structure analysis displayed a 1:1 ratio. Crystal data are displayed in Table 3. Selected bond lengths and angles are presented in Figure 5. ^{1}H NMR, H–H COSY ($CDCl_3$): δ = 0.50–1.80 (v. br. m, 3 H, BH_3), 1.36 (d, $^3J_{PH}$ = 13.7 Hz, 4 H, CMe_{3B}), 1.41 (d, $^3J_{PH}$ = 13.9 Hz, 5 H, CMe_{3B}), 2.34 (1.3 H, *p*-CH_{3B}), 2.42 (1.7 H, *p*-CH_{3A}), 4.67 (s, 0.54 H, OH_A), 4.73 (s, 0.44 H, OH_B), 6.37 (dd, ^3J = 7.6, ^4J = 1.6 Hz, 6-H_A), 6.49 (dd, ^3J = 8.1, ^4J = 0.7 Hz, 3-H_B), 6.51 (td, ^3J = 7.6, 7.4, ^4J = 0.9 Hz, 5-H_A), 6.67 (dd, ^3J = 8, ^4J = 1 Hz, 3-H_A), 6.69 (td, ^3J = 7.5, ^4J = 0.9 Hz, 5-H_B), 6.99

(superimposed td, $^3J \approx 7.8$, $^4J = 1.6$ Hz, 4-H_B), 7.00–7.10 (m, 4-H_A, 4 *m*-H_{AB}), 7.19 (dd, $^3J = 7.6$, $^4J = 1.6$ Hz, 6-H_B), 7.24 (ddd, $^3J = 7.5$, $^4J_{PH} = 3.4$, $^4J = 1.7$ Hz, 6′-H_B), 7.32 (ddd, $^3J = 7.5$, $^4J_{PH} = 3.4$, $^4J = 1.7$ Hz, 6′-H_A), 7.39 (dd, $^3J = 8.1$, $^3J_{PH} = 5.4$ Hz, 2 *o*-H_A), 7.43 (dd, $^3J = 8.0$, $^3J_{PH} = 5.4$ Hz, 2 *o*-H_B), 7.51–7.63 (m, 4 H, 4′-H_{AB}, 5′-H_{AB}), 8.10–8.18 (m, 3′-H_B), 8.21–8.29 (m, 3′-H_A) ppm. $^{13}C\{^1H\}$ NMR, C–H COSY ($CDCl_3$): $\delta = 21.26$ (*p*-Me_B), 21.37 (*p*-Me_A), 27.23 (d, $^2J = 2.3$ Hz, C*Me*$_{3A}$), 27.57 (d, $^2J = 2.2$ Hz, C*Me*$_{3B}$), 31.66 (d, $^1J = 31.1$ Hz, *C*Me$_{3A}$), 32.28 (d, $^1J = 31.0$ Hz, *C*Me$_{3B}$), 114.89 (C-3$_A$), 116.66 (C-3$_B$), 119.36 (C-5$_{AB}$), 124.33 (d, $^1J = 54.1$ Hz, 2 C_q-*i*$_{AB}$), 127.37 (d, $^3J = 9.1$ Hz, C-4′$_A$), 127.41 (d, $^3J = 9.1$ Hz, C-4′$_B$), ca. 127.4 (superimposed C_q-1$_A$), 127.51 (d, $^3J \approx 4$ Hz, C_q-1$_B$), 128.38 (d, $^3J = 10.3$ Hz, 2 C-*m*$_A$), 128.50 (d, $^3J = 10.2$ Hz, 2 C-*m*$_B$), 128.82 (C-4$_A$), 129.04 (C-4$_B$), 129.27 (br. d, $^1J \approx 52$ Hz, C_q-2′$_A$), 130.36 (d, $^4J = 2.3$ Hz, C-5′$_B$), 130.83 (d, $^4J = 2.2$ Hz, C-5′$_A$), 130.6 (superimposed d, $^1J \approx 59$ Hz, C_q-2′$_B$, tentatively), 132.12 (C-6$_B$), 132.90 (d, $^2J = 8.5$ Hz, C-*o*$_B$), 133.25 (d, $^3J = 7.2$ Hz, C-6′$_A$), 133.79 (d, $^2J = 8.8$ Hz, C-3′$_A$), 134.15 (d, $^3J = 7$ Hz, C-6′$_B$), 134.16 (d, $^2J = 8.8$ Hz, C-*o*$_A$), 134.63 (d, $^2J = 8.6$ Hz, C-3′$_B$), 140.53 (d, $^2J = 2.5$ Hz, C_q-1′$_B$), 140.91 (d, $^2J = 2.5$ Hz, C_q-1′$_A$), 141.80 (d, $^4J = 5.7$ Hz, C_q-*p*$_A$), 141.98 (d, $^4J = 5.5$ Hz, C_q-*p*$_B$), 151.33 (C_q-2$_B$), 152.87 (C_q-2$_A$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 33.0$ (pseudo-d, A), 35.1 (pseudo-d, B); trace impurity signal at $\delta = 7.04$ ppm. MS (EI, 70 eV, 150 °C): *m*/*z* (%) = 363 (5), 362 (17) $[M]^+$, 348 (7), 332 (21), 331 (100), 291 (11), 275 (59), 272 (10), 200 (8), 199 (66), 183 (23), 151 (11), 57 (15). $C_{23}H_{28}BOP$ (362.25): calcd. C 76.26, H 7.79; found C 75.94, H 7.72.

2-Hydroxy-2′-[mesityl(methyl)phosphanyl]-1,1′-biphenyl (5c) and the Borane Adduct 6c: The silyl ether **2c** (2.12 g, 5.21 mmol) was heated at reflux in methanol (15 mL) for 4 h. Then the solvent was removed in vacuo, the residual crude **5c** dissolved in CH_2Cl_2 (10 mL), the solution cooled to –80 °C, and a solution of $H_3B{\cdot}SMe_2$ in dichloromethane (6.0 mL, 6.0 mmol) added. After warming to room temperature, the mixture was stirred for 4 h to complete the reaction. Then the solvent was evaporated and the product purified by column chromatography on silica gel with CH_2Cl_2/hexane (1:1) to yield 0.83 g (46%) of a viscous liquid product. The NMR spectra indicate a diastereoisomer ratio A/B of 67:33 to 62:38 based on ^1H NMR integration and ^{13}C NMR intensities of related signals. ^1H NMR ($CDCl_3$): $\delta = 0.50$–1.80 (v. br. m, 3 H, BH_3), 1.77 (d, $^2J_{PH} = 9.7$ Hz, 2 H, PMe_A), 1.82 (d, $^2J_{PH} = 9.5$ Hz, 1 H, PMe_B), 2.12 (4 H, *o*-CH_{3A}), 2.15 (2 H, *o*-CH_{3B}), 2.22 (2 H, *p*-CH_{3A}), 2.24 (1 H, *p*-CH_{3B}), 4.52 (s, 0.65 H, OH_A), 4.57 (s, 0.35 H, OH_B), 6.52 (br. d, $^3J = 5$ Hz, 0.65 H, 3-H_A), 6.54 (td, $^3J = 7.5$, $^4J = 1.1$ Hz, 0.65 H, 5-H_A), 6.63–6.73 (m, 3.35 H, 5-H_B, 6-H_{AB}, 2 *m*-H_{AB}), 6.80 (br. d, $^3J = 8.1$ Hz, 0.35 H, 3-H_B), 7.07 (td, $^3J = 7.5$, $^4J = 1.7$ Hz, 0.63 H, 4-H_A), 7.13 (ddd, $^3J \approx 7$, $^4J_{PH} \approx 4$, $^4J \approx 1$ Hz, 0.37 H, 6′-H_B), 7.17–7.24 (m, 1 H, 6′-H_A, 4-H_B), 7.45–7.56 (m, 2 H, 4′-H_{AB}, 5′-H_{AB}), 7.71–7.80 (m, 0.38 H, 3′-H_B), 7.97–8.08 (m, $^3J_{PH} = 13.8$ Hz, 0.62 H, 3′-H_A) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.40$ (d, $^1J = 42.0$ Hz, PMe_B), 16.05 (d, $^1J = 41.7$ Hz, PMe_A), 20.74 (*p*-Me_A), 20.80 (*p*-Me_B), 23.37 (d, $^3J = 5.4$ Hz, *o*-Me_B), 23.51 (d, $^3J = 5.5$ Hz, *o*-Me_A), 115.04 (C-3$_A$), 116.27 (C-3$_B$), 119.59 (C-5$_B$), 119.72 (C-5$_A$), 123.60 (d, $^1J = 52$ Hz, C_q-*i*$_B$), 123.71 (d, $^1J = 52.0$ Hz, C_q-*i*$_A$), 126.59 (d, $^3J = 3.2$ Hz, C_q-1$_A$), 127.0 (d, $^3J = 3$ Hz, C_q-1$_B$), 128.5 (d, $^3J = 10$ Hz, C-4′$_B$), 128.56 (d, $^3J = 11.3$ Hz, C-4′$_A$), 129.34 (s, C-4$_A$), 129.42 (s, C-4$_B$), 130.36 (d, $^4J = 2.2$ Hz, C-5′$_B$), 130.67 (br. s, 2 *m*-CH), 130.80 (C-6$_A$), 130.81 (d, $^4J = 2.3$ Hz, C-5′$_A$), 131.45 (d, $^2J = 10.5$ Hz, C-3′$_B$), 132.09 (d, $^3J = 6.6$ Hz, C-6′$_A$), 132.62 (d, $^4J = 7.7$ Hz, C-6′$_B$), 133.39 (d, $^2J = 14.6$ Hz, C-3′$_A$), 134.59 (d, $^1J = 53.0$ Hz, C_q-2′$_A$), 134.65 (d, $^1J = 53$ Hz, C_q-2′$_B$), 139.71 (d, $^2J = 3.8$ Hz, C_q-1′$_B$), 139.97 (d, $^2J = 7.2$ Hz, C_q-1′$_A$), 140.43 (*p*-C_A), 140.90 (*p*-C_B), 142.47 (d, $^2J = 9.3$ Hz, *o*-C_A), 143.50 (d, $^2J = 9.5$ Hz, *o*-C_B), 152.35 (C-2$_A$), 152.98 (C-2$_B$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 9.8$ (br. m, B), 12.5 (br. m, A); trace impurity signal at $\delta = -39.5$ ppm. MS (EI, 70 eV, 345 °C): *m*/*z* (%) = 348 (0.3) $[M]^+$, 334 (27), 316 (26), 317 (94), 199 (19), 119 (18), 105 (27), 74 (100). $C_{22}H_{26}BOP$ (348.23): calcd. C 75.88, H 7.53; found C 75.63, H 7.67.

2-Hydroxy-2′-(dimethylphosphanyl)-1,1′-biphenyl (5e): Compound **2e** (959 mg, 3.17 mmol) was dissolved in methanol (15 mL) and stirred at room temperature overnight. Then the solvent was removed in vacuo to yield 728 mg (100%) of a colourless solid. ^1H NMR ($CDCl_3$): $\delta = 1.12$ (br. s, 3 H, PMe_A), 1.19 (br. s, 3 H, PMe_B), 5.15 (v. br. s, 1 H, OH), 6.99 (td, $^3J = 7.4$, $^4J = 1.2$ Hz, 1 H, 5-H), 7.00 (br. dd, $^3J = 8$, $^4J = 1.6$, $^5J \approx 0.4$ Hz, 1 H, 3-H), 7.17 (ddd, $^3J = 7.4$, $^4J = 1.8$, $^5J \approx 0.3$ Hz, 1 H, 6-H), 7.23–7.27 (m, 1 H, 6′-H), 7.30 (td, $^3J = 8.2$, 7.3, $^4J = 1.7$ Hz, 1 H, 4-H), 7.40 (m, $^3J \approx 7.5$, $^4J = 1.6$ Hz, 1 H, 5′-H or 4′-H), 7.44 (m, $^3J \approx 7.5$, $^4J = 1.6$ Hz, 1 H, 4′-H or 5′-H), 7.55 (ddd, $^3J_{PH} = 3.7$, $^3J = 6.9$, $^4J = 1.7$ Hz, 1 H, 3′-H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -49.7$ (br.); trace impurity phosphane oxide signal at $\delta = 41.0$ ppm. For the analytical characterization as a borane adduct, see below.

2-Hydroxy-2′-(dimethylphosphanyl)-1,1′-biphenyl–Borane (6e): A solution of $H_3B{\cdot}SMe_2$ in dichloromethane (3.5 mL, 1 M, 3.50 mmol) was added at –60 °C to a solution of **5e** (728 mg, 3.16 mmol) in the same solvent (10 mL). The mixture was warmed to room temperature and stirred overnight. Then the solvent was removed in vacuo and the product crystallized from methanol to yield 700 mg (91%) of colourless crystals, m.p. 128–131 °C (decomposition). Crystal data are displayed in Table 3. Selected bond lengths and angles are presented in Figure 7. ^1H NMR, H–H COSY ($CDCl_3$): $\delta = 0.15$–1.20 (v. br. pseudo-q, 3 H, BH_3), 1.27 (d, $^2J_{PH} = 10.5$ Hz, 3 H, PMe_A), 1.29 (d, $^2J_{PH} = 10.5$ Hz, 3 H, PMe_B), 4.69 (s, 1 H, OH), 6.98 (br. dd, $^3J = 8.0$, $^4J = 1.0$ Hz, 1 H, 3-H), 7.00 (td, $^3J = 7.5$, 7.6, $^4J = 1.0$ Hz, 1 H, 5-H), 7.16 (dd, $^3J = 7.5$, $^4J = 1.8$ Hz, 6-H), 7.28 (ddd, $^3J \approx 7.2$, $^4J_{PH} \approx 2.7$, $^4J = 1.7$ Hz, 1 H, 6′-H), 7.34 (td, $^3J = 8.1$, 7.6, $^4J = 1.8$ Hz, 1 H, 4-H), 7.51 (tt, $^3J = 7.5$, $^4J \approx {}^4J_{PH} = 1.7$ Hz, 1 H, 4′-H), 7.57 (tt, $^3J = 7.4$, $^4J \approx {}^5J_{PH} = 1.6$ Hz, 1 H, 5′-H), 8.10 (ddd, $^3J_{PH} = 13.8$, $^3J = 7.4$, $^4J = 1.6$ Hz, 1 H, 3′-H) ppm. $^{13}C\{^1H\}$ NMR, C–H COSY ($CDCl_3$): $\delta = 12.36$ (d, $^1J = 39.9$ Hz, PMe_B), 13.70 (d, $^1J = 39.3$ Hz, PMe_A), 115.93 (C-3), 120.20 (C-5), 127.16 (d, $^3J = 2.8$ Hz, C_q-1), 128.61 (d, $^3J = 12.1$ Hz, C-4′), 130.37 (C-4), 130.55 (d, $^1J = 49.9$ Hz, C_q-2′), 131.07 (C-6), 131.50 (d, $^4J = 2.4$ Hz, C-5′), 132.06 (d, $^3J = 6.3$ Hz, C-6′), 134.99 (d, $^2J = 17.2$ Hz, C-3′), 140.15 (d, $^2J = 1.7$ Hz, C_q-1′), 152.86 (C_q-2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 6.8$ (pseudo-q) ppm. MS (EI, 70 eV, 300 °C): *m*/*z* (%) = 244 (6) $[M]^+$, 243 (6), 241 (15), 214 (16), 213 (100), 183 (14), 151 (8). $C_{14}H_{18}BOP$ (244.08): calcd. C 68.89, H 7.43; found C 68.84, H 7.20.

2-(Di-*o*-anisylphosphanyl)-2-hydroxy-1,1′-biphenyl (5f): Compound **2f** (0.730 g, 1.5 mmol) was heated at reflux in methanol (20 mL) for 1 week. Then the precipitate formed during heating was separated by filtration at room temperature, washed with a small amount of methanol and dried in vacuo to yield 0.338 g (54%) of white crystals, m.p. 160–161 °C. ^1H NMR ($CDCl_3$): $\delta = 3.61$, 3.77 (2 s, each 3 H, 2′′-OMe), 6.53 (v. br. t, 1 H, 3′′-H), 6.78–6.93 [partly resolved superimposed multiplets: 6.79 (td, $^3J = 7.4$, $^4J = 1.1$ Hz), 6.83 (br. t), 6.88 (td, $^3J = 7.4$, $^4J = 1.1$ Hz), 7 H, aryl], 7.02–7.09 (m, 2 H, aryl), 7.20 (td, $^3J = 8.2$, 7.3, $^4J = 1.8$ Hz, 1 H, aryl), 7.27–7.39 (m, 4 H, aryl), 7.48 (td, $^3J = 7.3$, $^4J \approx 1$ Hz, 1 H, aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -32.0$ (br.) ppm. MS (EI, 70 eV): *m*/*z* (%) = 415 (15) $[M]^+$, 414 (8), 398 (30), 397 (100), 381 (6), 367 (5), 351 (9). $C_{26}H_{23}O_3P$ (414.43): calcd. C 75.35, H 5.59; found C 75.41, H 5.76.

2-[Bis(2,4-dimethoxyphenyl)phosphanyl]-2-hydroxy-1,1′-biphenyl (5g) via Silyl Ether 2g: A solution of *t*BuLi (3.20 mL, 1.5 M in hexane, 4.74 mmol) was added dropwise at –70 °C to 1-bromo-2,4-dimethoxybenzene (0.68 mL, 4.74 mmol) dissolved in diethyl ether (10 mL), and the mixture was stirred at 20 °C for 2 h. The turbid solution of 2,4-dimethoxyphenyllithium was added at –80 °C to a solution of **1$_{Cl}$** (506 mg, 2.16 mmol) in diethyl ether (10 mL). The reaction mixture was warmed to room temperature and stirred overnight. Then $ClSiMe_3$ (0.62 mL, 4.89 mmol) was added. After 2 h at room temperature, the precipitate was filtered off and the solvent removed in vacuo to give crude viscous liquid **2g**. This was dissolved in excess methanol (20 mL) and heated at reflux for 6 h to complete the methanolysis of the silyl ether (NMR control). The precipitate formed was separated and dried in vacuo to give 370 mg (36%) of white crystals, m.p. 175–176 °C. ^{1}H NMR (CD_2Cl_2): δ = 3.62, 3.73, 3.77, 3.80 (br. s, each 3 H, 2′′,4′′-OMe), 5.94 (d, J = 3.5 Hz, 1 H, OH), 6.38 (br. s, 2 H, 3′′-H), 6.40–6.50 (br. m, 3 H, 2 5′′-H, 6′′-H), 6.65 (br. dd, ^3J = 8.1, $^3J_{PH}$ = 4.5 Hz, 6′′-H), 6.84 (td, ^3J = 7.4, 7.3, ^4J = 1.1 Hz, 1 H, 5-H), 6.92 (dd, ^3J = 7.5, ^4J = 1.8 Hz, 1 H, 6-H), 6.97 (dd, ^3J = 8.1, ^4J = 1.1 Hz, 1 H, 3-H), 7.03 (ddd, $^3J_{PH}$ = 3.7, ^3J = 6.9, ^4J = 1.7 Hz, 1 H, 3′-H), 7.23 (td, ^3J = 8.1, 7.4, ^4J = 1.8 Hz, 1 H, 4-H), 7.23 (dd, ^3J = 7.3, ^4J = 1.5 Hz, 1 H, 6′-H), 7.30 (td, ^3J = 7.5, ^4J = 1.4 Hz, 1 H, 5′-H or 4′-H), 7.45 (td, ^3J = 7.4, 7.5, ^4J = 1.3 Hz, 1 H, 4′-H or 5′-H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 55.62, 55.90, 56.12 (2′′,4′′-OMe), 98.46, 98.73 (2 br. s, C-3′′), 105.77 (2 C-5′′), 115.0 (br. d, $^1J \approx$ 10 Hz, C_q-1′′), 116.2 (br. d, $^1J \approx$ 10 Hz, C_q-1′′), 117.03 (C-3), 120.83 (C-5), 128.57, 129.43, 129.92 (C-4, C-4′, C-5′), 130.23 (d, ^3J = 6.0 Hz, C_q-1), 131.16 (d, ^3J = 1.8 Hz, C-3′), 131.44 (d, ^3J = 6.1 Hz, C-6′), 134.12, 135.14 (2 br. s, C-6′′), 134.54 (C-6), 137.33 (d, ^1J = 11.7 Hz, C_q-2′), 143.88 (d, ^2J = 35.1 Hz, C_q-1′), 152.88 (d, ^4J = 1.2 Hz, C-2), 161.81, 162.33, 162.53 (superimposed br. d and s, C-2′′, C-4′′) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, ref. ext. $CDCl_3$): δ = –34.4 ppm. MS (EI, 70 eV, 135 °C): *m*/*z* (%) = 474 (16) [M]$^+$, 473 (9), 458 (27), 457 (100), 243 (11), 215 (11), 199 (14), 197 (15), 170 (28). $C_{28}H_{27}O_5P$ (474.48): calcd. C 70.88, H 5.74; found C 70.99, H 5.46.

2-Acetoxy-2′-[*tert*-butyl(methyl)phosphanyl]-1,1′-biphenyl (7a): $NaHCO_3$ (0.764 g) was added to a solution of **5a** (0.248 g, 0.91 mmol) in diethyl ether (10 mL) followed by dropwise addition of acetyl chloride (0.13 mL, 1.82 mmol). After stirring the mixture overnight, the precipitate was filtered off, the filtrate was washed with water (3 × 2 mL), and the organic layer dried with Na_2SO_4. Solvent evaporation in vacuo yielded 0.195 g (68%) of the pure product as a viscous liquid. Diastereoisomeric ratio A/B based on ^{1}H NMR integration and ^{13}C NMR intensities of separated related signals ca. 70:30. ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, $^3J_{PH}$ = 12.0 Hz, 6.3 H, CMe_{3A}), 0.86 (d, $^3J_{PH}$ = 12.2 Hz, 2.7 H, CMe_{3B}), 1.29 (d, $^2J_{PH}$ = 5.5 Hz, 0.9 H, PMe_B), 1.32 (d, $^2J_{PH}$ = 5.3 Hz, 2.1 H, PMe_A), 1.85 (s, Me_A), 2.04 (s, Me_B), 7.11 (dm, ^3J = 8.0 Hz, 1 H, 3-H), 7.19–7.25 (m, 1 H, 5-H), 7.27–7.36 (m, 2 H, 6′-H, 6-H), 7.36–7.44 (m, 3 H, 4-H, 5′-H, 4′-H), 7.55–7.65 (m, 1 H, 3′-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 6.36 (d, ^1J = 18.9 Hz, PMe_B), 6.57 (d, ^1J = 19.8 Hz, PMe_B), 20.35 (Me_A), 20.69 (Me_B), 26.85 (d, ^2J = 14.0 Hz, CMe_{3B}), 27.03 (d, ^2J = 14.3 Hz, CMe_{3A}), 28.98 (d, ^1J = 12.9 Hz, CMe_{3B}), 29.41 (d, ^1J = 12.3 Hz, CMe_{3A}), 121.63 (C-3_A), 122.56 (C-3_B), 124.71 (C-5_B), 125.51 (C-5_A), 126.79, 127.98, 128.16, 128.49, 128.82 (C-5′$_{AB}$, C-4′$_{AB}$, C-4$_{AB}$), 129.74 (d, ^3J = 5.2 Hz, C-3′$_B$), 130.50 (d, ^3J = 6.4 Hz, C-3′$_A$), 131.13 (d, ^2J = 3.6 Hz, C-6_A), 131.52 (C-6′$_{AB}$), 132.10 (d, ^2J = 2.9 Hz, C-6_B), 133.66 (d, ^3J = 7.6 Hz, C_q-1$_A$), 134.59 (d, $^3J \approx$ 5 Hz, C_q-1$_B$), 136.06 (d, ^1J = 6.5 Hz, C_q-2′$_A$), 136.32 (br., C_q-2′$_B$), 144.48 (d, ^2J = 33.3 Hz, C-1′$_A$), 144.40 (d, ^2J = 33 Hz, C-1′$_B$), 147.67 (C-2_A), 148.14 (C-2_B), 168.59 (C=O_A), 169.77 (C=O_B) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –21.4, –25.5 (intensity ratio A/B > 75:25), trace impurity signals at δ = 51.6, 50.3 ppm (2:1, phosphane oxides). MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 313 (1) [M – 1]$^+$, 256 (16), 255 (88) [M – OC(O)Me]$^+$, 215 (16), 200 (17), 199 (100) [M – OC(O)Me – C_4H_8]$^+$, 183 (13), 151 (9), 74 (17), 57 (21), 43 (22). $C_{19}H_{23}O_2P$ (314.36): calcd. C 72.59, H 7.37; found C 72.68, H 7.61.

2-Acetoxy-2′-[*tert*-butyl(methyl)phosphanyl]-1,1′-biphenyl–Borane (8a): Reaction of $H_3B{\cdot}SMe_2$ in dichloromethane (4.38 mL, 1 M, 4.38 mmol) with **7a** (1.312 g, 4.17 mmol) in CH_2Cl_2 (5 mL) at –70 to 20 °C overnight, removal of the solvent in vacuo and purification by column chromatography on silica gel by using dichloromethane/*n*-hexane (1:1) as eluent furnished 0.406 g (30%) of pure **8a** as colourless crystals, m.p. 92–96 °C. Diastereoisomeric ratio A/B based on ^{1}H NMR integration and ^{13}C NMR intensities of separated related signals ca. 80:20–85:15. ^{1}H NMR ($CDCl_3$): δ = 0.15–1.20 (v. br. m, 3 H, BH_3), 0.99 (superimposed d, $^2J_{PH}$ = 11–12 Hz, 3 H, PMe), 1.03 (d, $^3J_{PH}$ = 13.7 Hz, 7.2 H, $PCMe_{3A}$), 1.07 (d, $^3J_{PH}$ = 13.7 Hz, 1.8 H, $PCMe_{3B}$), 1.84 (s, Me_A), 1.97 (s, Me_B), 7.11 (d, ^3J = 8.0 Hz, 1 H, 3-H), 7.10–7.20 (m, 2 H, 5-H, 6-H), 7.32 (dd, ^3J = 7.5, $^4J_{PH}$ = 11.6 Hz, 1 H, 6′-H), 7.40–7.49 (m, 3 H, 4-H, 4′-H, 5′-H), 7.98–8.11 (m, $^3J_{PH} \approx$ 13 Hz, 1 H, 3′-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 5.40 (d, ^1J = 36.5 Hz, PMe_A), 7.81 (d, ^1J = 37.0 Hz, PMe_B), 20.16 (Me_A), 20.58 (Me_B), 25.72 (d, ^2J = 2.5 Hz, CMe_{3A}), 25.76 (superimposed d, ^2J = 4.7 Hz, CMe_{3B}), 29.76 (d, ^1J = 32.6 Hz, CMe_{3A}), 29.99 (d, ^1J = 32.1 Hz, CMe_{3B}), 122.41 (C-3_A), 122.91 (C-3_B), 125.40 (d, ^1J = 48.9 Hz, C-2′$_A$), 125.68 (C-5_A), 126.3 (d, ^1J = 49 Hz, C-2′$_B$), 126.32 (C-5_B), 127.0 (superimposed d, ^3J > 9 Hz, C-4′$_B$), 127.08 (d, ^3J = 12.3 Hz, C-4′$_A$), 129.47 (C-4_B), 129.57 (C-4_A), 129.91 (C-1_B), 130.27 (d, ^3J = 2.3 Hz, C-1_A), 130.83 (C-6_A), 133.8 (br., C-5′$_B$), 134.89 (d, ^4J = 2.5 Hz, C-5′$_A$), 131.57 (d, ^3J = 6.5 Hz, C-6′$_B$), 132.12 (d, ^3J = 6.1 Hz, C-6′$_A$), 132.71 (C-6_B), 136.03 (d, ^2J = 16.9 Hz, C-3′$_{AB}$), 140.32 (C-1′$_A$), 141.59 (C-1′$_B$), 148.07 (C-2_B), 148.99 (C-2_A), 168.84 (C=O_A), 169.29 (C=O_B) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 33.5 (br., A and B unresolved) ppm. MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 328 (0.2) [M]$^+$, 314 (0.7), 285 (0.7), 283 (3.5), 267 (5.5), 256 (19), 255 (100), 215 (8), 199 (51), 183 (13), 179 (6), 151 (6), 103 (9), 57 (14). $C_{19}H_{26}BO_2P$ (328.19): calcd. C 69.53, H 7.99; found C 69.67, H 8.13.

2-Acetoxy-2′-(di-*o*-anisylphosphanyl)-1,1′-biphenyl (7f): A solution of *n*BuLi (1.5 mL, 1.6 M solution in hexane, 2.40 mmol) was added dropwise to a solution of **2f** (1.113 g, 2.29 mmol) in toluene (15 mL) at –78 °C. The reaction mixture was warmed to room temperature. After 2 h, a solution of acetyl chloride (0.17 mL, 2.40 mmol) in diethyl ether (5 mL) was added at –78 °C, and stirring was continued at room temperature overnight. The precipitate was then filtered off, and the solution was washed with water and dried with $MgSO_4$. After solvent evaporation, a yellow viscous liquid was formed that crystallized after addition of dichloromethane with 2/3CH_2Cl_2 per molecule. ^{1}H NMR, H–H COSY ($CDCl_3$): δ = 1.91 (s, 3 H, Me), 3.62, 3.66 (s, 6 H, 2′′-OMe), 5.30 (s, 1.3 H, 0.67 CH_2Cl_2), 6.70–6.77 (br. m, 2 H, 6′′-H), 6.77–6.88 (br. m, 4 H, 3′′-CH, 5′′-CH), 7.05 (dt, ^3J = 8.0, $^4J \approx {}^3J_{PH}$ = 0.5–0.8 Hz, 1 H, 6′-H), 7.07 (dd, ^3J = 8.1, ^3J = 1.4 Hz, 1 H, 3-H), 7.09–7.13 (superimposed "d", 2 H, 5-CH, 6-CH), 7.21 (d, 1 H, 3′-H), 7.22 (t, 1 H, 5′-H), 7.29 (tm, 2 H, 4′′-H), 7.31 (t, 1 H, 4-H), 7.34 (t, 1 H, 4′-H) ppm. ^{13}C{^{1}H} NMR, C–H COSY ($CDCl_3$): δ = 20.63 (Me), 55.40, 55.54 (2 s, OMe), 110.10, 110.18 (2 s, 2 C-3′′), 120.65 (s, 2 C-5′′), 122.24 (s, C-3), 125.23 (C-5), 125.01 (d, $^1J_{PC}$ = 15.2 Hz, 1 C_q-*i*), 125.67 (d, $^1J_{PC}$ = 13.2 Hz, 1 C_q-*i*), 127.51 (s, C-5′), 128.05 (s, C-4′), 128.43 (s, C-4), 129.71 (d, $^2J_{PC}$ = 5.3 Hz, C-3′), 129.82 (br. s, 2 C-4′′), 131.70 (d, $^4J_{PC}$ = 3.7 Hz, C-6), 133.86 (s, C-6′), 134.11 (br. s, 2 C-6′′), 134.67 (d, $^3J_{PC}$ = 6.8 Hz, C_q-1), 136.49 (d, $^1J_{PC}$ = 12.1 Hz, C_q-2′), 143.26 (d, ^2J = 31.7 Hz, C-1′), 161.28 (br. d, $^2J_{PC}$

Table 3. Crystallographic data.

	3·3C_6D_6	**5c$_{Ox}$**·1/2H_2O	**6b**	**6e**
Empirical formula	$C_{34}H_{19}D_{18}O_2P$	$C_{22}H_{24}O_{2.5}P$	$C_{23}H_{28}BOP$	$C_{14}H_{18}BOP$
M_t	526.72	359.38	362.23	244.06
T [K]	133(2)	133(2)	133(2)	133(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$Pna2_1$	$P2_1/n$
a [Å]	9.8433(8)	23.110(2)	14.5556(12)	9.9297(4)
b [Å]	12.5272(11)	11.0977(11)	8.8905(8)	8.5673(4)
c [Å]	13.1816(11)	14.9704(15)	31.443(3)	16.1589(7)
α [°]	70.398(4)	90	90	90
β [°]	86.451(4)	99.779(3)	90	98.124(1)
γ [°]	71.655(4)	90	90	90
V [Å^3]	1451.7(2)	3783.6(6)	4069.0(6)	1360.85(10)
Z	2	8	8	4
$\rho_{calcd.}$ [Mg/m^3]	1.227	1.262	1.183	1.191
μ [mm^{-1}]	0.12	0.16	0.14	0.18
F(000)	544	1528	1552	520
Crystal size [mm]	0.34 × 0.28 × 0.26	0.3 × 0.2 × 0.2	0.35 × 0.25 × 0.15	0.35 × 0.20 × 0.15
θ range [°]	1.64–28.28	1.79–30.51	1.30–30.51	2.27–30.51
Index ranges	$-13 \le h \le 13$	$-32 \le h \le 32$	$-20 \le h \le 20$	$-13 \le h \le 14$
	$-16 \le k \le 16$	$-15 \le k \le 15$	$-12 \le k \le 12$	$-12 \le k \le 12$
	$-17 \le l \le 17$	$-21 \le l \le 21$	$-44 \le l \le 44$	$-23 \le l \le 23$
Collected reflections	20782	21939	69887	17388
Independent reflections	7173	5768	12413	4143
R(int)	0.062	0.055	0.047	0.042
Completeness to ϕ = 30.00° [%]	99.6	99.9	100.0	99.8
Data/restraints/parameters	7173/0/345	5768/0/243	12413/9/510	4143/0/172
GOF on F^2	0.98	1.04	1.00	1.06
Final R indices	$R1$ = 0.0394	$R1$ = 0.0463	$R1$ = 0.0398	$R1$ = 0.0376
[$I > 2\sigma(I)$]	$wR2$ = 0.0905	$wR2$ = 0.1139	$wR2$ = 0.0954	$wR2$ = 0.0966
R indices	$R1$ = 0.0675	$R1$ = 0.0621	$R1$ = 0.0585	$R1$ = 0.0459
(all data)	$wR2$ = 0.0997	$wR2$ = 0.1216	$wR2$ = 0.1028	$wR2$ = 0.1013
Largest difference peak/hole [e/Å^3]	0.44/–0.30	0.45/–0.26	0.44/–0.20	0.51/–0.20

= 18.1 Hz, C_q-2′′), 148.06 (C_q-2), 169.59 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = –34.3 (br.) ppm. MS (EI, 70 eV, 345 °C): m/z (%) = 456 (1) $[M]^+$, 427 (2), 398 (32), 397 (100), 367 (6), 151 (14), 229 (4), 199 (15), 44 (19), 43 (17). $C_{28}H_{25}O_4P$ (456.15): calcd. C 73.67, H 5.52; for the 2/3CH_2Cl_2 solvate C 67.10, H 5.15; found C 66.93, H 5.35.

Crystal Structure Analyses: Crystals of **3**, **5c$_{Ox}$**, **6b** and **6e** were mounted on glass fibres in inert oil. Data were recorded at low temperature with a Bruker SMART 1000 CCD diffractometer by using Mo-K_α-radiation (λ = 0.71073 Å). No absorption corrections were applied. Selected bond lengths and angles for **6b** are presented in Figures 3–5 and 7 and in Tables 1 and 2, and crystal data are presented in Table 3. The structures were solved by direct methods and refined by full-matrix least squares on F^2.[25] The hydrogen atoms of the BH, PH and OH groups were refined freely. Methyl H atoms were included as rigid idealized methyl groups. Other H atoms were included by using a riding model. Special features: for **6b**, the Flack parameter refined to 0.04(6). Sets of O–H, B–H (hydrogen-bonded) and B–H (not hydrogen-bonded) distances were restrained equal. CCDC-784400 (**3**), -784401 (**5c$_{Ox}$**), -784402 (**6b**) and -784403 (**6e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected ^{1}H, ^{31}P and/or ^{13}C NMR spectra of compounds **1**–**8**, H–H and C–H COSY spectra of **1$_{Mes}$**, **2a**, **2b**, **6e** and **7f**, data on hydrogen bonds and figures of the packing in the crystal for **3**, **5c$_{Ox}$**, **6b** and **6e** and description of the oligo/polymerization of ethylene by catalysts formed in situ from [Ni(cod)$_2$] and 2-hydroxyphenylphosphane–boranes.

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[1] a) D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; b) R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473, and references cited therein.
[2] D. S. Glueck, *Chem. Eur. J.* **2008**, *14*, 7108–7117.
[3] a) Y. Uozumi, A. Tanahashi, S. Y. Lee, T. Hayashi, *J. Org. Chem.* **1993**, *58*, 1945–1948; b) Y. Uozumi, N. Suzuki, A. Ogiwara, T. Hayashi, *Tetrahedron* **1994**, *50*, 4293–4310.
[4] a) M. Shi, C.-Q. Li, *Tetrahedron: Asymmetry* **2005**, *16*, 1385–1391; b) M. Shi, L.-A. Chen, C.-Q. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3790–3800; c) K. Matsui, T. H. Sasai, *Synlett* **2006**, 761–765; d) K. Ito, K. Nishida, T. Gotanda, *Tetrahedron Lett.* **2007**, *48*, 6147–6149; e) X. Meng, Y. Huang, R. Chen, *Chem. Eur. J.* **2008**, *14*, 6852–6856; f) X. Meng, Y. Huang, R. Chen, *Org. Lett.* **2009**, *11*, 137–140.
[5] R. Kadyrov, J. Heinicke, M. K. Kindermann, D. Heller, C. Fischer, R. Selke, A. K. Fischer, P. G. Jones, *Chem. Ber./Recueil* **1997**, *130*, 1663–1670.
[6] M. An der Heiden, H. Plenio, *Chem. Eur. J.* **2004**, *10*, 1789–1797.

[7] Y. Luo, F. Wang, G. Zhu, Z. Zhang, *Tetrahedron: Asymmetry* **2004**, *15*, 17–19.
[8] J. Heinicke, W. Wawrzyniak, N. Peulecke, B. R. Aluri, M. K. Kindermann, P. G. Jones, S. Enthaler, M. Beller, *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 224–232.
[9] a) G. Keglevich, A. Kerényi, H. Szelke, K. Ludányi, T. Körtvélyesi, *J. Organomet. Chem.* **2006**, *691*, 5038–5044; b) G. Keglevich, H. Szelke, A. Kerényi, T. Imre, K. Ludányi, J. Dukai, F. Nagy, P. Arányi, *Heteroat. Chem.* **2004**, *15*, 459–463.
[10] a) E. A. Chernyshev, E. F. Bugerenko, V. I. Aksenov, *Zh. Obshch. Khim.* **1971**, *41*, 800–804; b) E. A. Chernyshev, V. I. Aksenov, V. V. Ponomarev, S. A. Golubtsov, E. F. Bugerenko, *Zh. Obshch. Khim.* **1972**, *42*, 93–96.
[11] a) T. Higashizima, N. Sakai, K. Nozaki, H. Takaya, *Tetrahedron Lett.* **1994**, *35*, 2023–2026; b) K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, *J. Am. Chem. Soc.* **1997**, *119*, 4413–4423; c) M. Beller, B. Zimmermann, H. Geissler, *Chem. Eur. J.* **1999**, *5*, 1301–1305.
[12] S. Haber, A. Meudt, A. Noerenberg, S. Scherer, F. Vollmueller (Clariant GmbH), German patent, DE 19920847 A1 (*Chem. Abstr.* **2000**, *126*, 785819).
[13] a) D. Selent, D. Röttger, K.-D. Wiese, A. Börner, *Angew. Chem. Int. Ed.* **2000**, *39*, 1639–1641; b) D. Selent, W. Baumann, R. Kempe, A. Spannenberg, D. Röttger, K.-D. Wiese, A. Börner, *Organometallics* **2003**, *22*, 4265–4271; c) I. A. Shuklov, N. V. Dubrovina, H. Jiao, A. Spannenberg, A. Börner, *Eur. J. Org. Chem.* **2010**, 1669–1680.
[14] F. Speiser, P. Braunstein, L. Saussine, *Dalton Trans.* **2004**, 1539–1545; J. Zhang, P. Braunstein, R. Welter, *Inorg. Chem.* **2004**, *43*, 4172–4177; M. Agostinho, P. Braunstein, R. Welter, *Dalton Trans.* **2007**, 759–770; A. Kermagoret, P. Braunstein, *Organometallics* **2008**, *27*, 88–99.
[15] a) G. Keglevich, H. Szelke, A. Kerényi, V. Kudar, M. Hanusz, K. Simon, T. Imre, K. Ludányi, *Tetrahedron: Asymmetry* **2005**, *16*, 4015–4021; b) A. Kerényi, A. Balassa, T. Körtvélyesi, K. Ludányi, G. Keglevich, *Transition Met. Chem.* **2008**, *33*, 459–465; c) G. Keglevich, A. Kerényi, B. Mayer, T. Körtvélyesi, K. Ludányi, *Transition Met. Chem.* **2008**, *33*, 505–510.
[16] J. Heinicke, R. Kadyrov, M. K. Kindermann, M. Koesling, P. G. Jones, *Chem. Ber.* **1996**, *129*, 1547–1560.
[17] a) N. Andrushko, A. Börner in *Phosphorus Ligands in Asymmetric Catalysis* (Ed.: A. Börner), Wiley-VCH, Weinheim, **2008**, vol. 3, pp. 1275–1347; b) A. C. Gaumont, B. Carboni, *Science Synth.* **2004**, *6*, 485–512; c) B. Carboni, L. Monnier, *Tetrahedron* **1999**, *55*, 1197–1248; d) M. Ohff, J. Holz, M. Quirmbach, A. Börner, *Synthesis* **1998**, 1391–1415; e) J. M. Brunel, B. Faure, M. Maffei, *Coord. Chem. Rev.* **1998**, *178–180*, 665–698.
[18] a) T. Imamoto, E. Hirakawa, Y. Yamanoi, T. Inoue, K. Yamaguchi, H. Seki, *J. Org. Chem.* **1995**, *60*, 7697–7700; b) D. Moulin, S. Bago, C. Bauduin, C. Darcel, S. Juge, *Tetrahedron: Asymmetry* **2000**, *11*, 3939–3956; c) C. J. Ngono, T. Constantieux, G. Buono, *J. Organomet. Chem.* **2002**, *643–644*, 237–246; d) N. Peulecke, J. Heinicke, unpublished results (see the Supporting Information).
[19] J.-P. Ebran, P. Jubault, X. Pannecouke, J.-C. Quirion, *Tetrahedron: Asymmetry* **2003**, *14*, 1637–1644.
[20] a) V. Sumerin, F. Schulz, M. Nieger, M. Atsumi, C. Wang, M. Leskelae, P. Pyykkoe, T. Repo, B. Rieger, *J. Organomet. Chem.* **2009**, *694*, 2654–2660; b) Y. Meng, Z. Zhou, C. Duan, B. Wang, Q. Zhong, *THEOCHEM* **2005**, *713*, 135–144; c) H. Crabtree in *Modern Coordination Chemistry* (Eds.: G. J. Leigh, N. Winterton), Royal Society of Chemistry, Cambridge, **2002**, pp. 31–44; d) R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963–1980; e) R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res.* **1996**, *29*, 348–354.
[21] J. C. Huffman, W. A. Skupinski, K. G. Caulton, *Cryst. Struct. Commun.* **1982**, *38*, 1435–1440.
[22] S. Philip, R. L. K. Bryan, *Inorg. Chem.* **1972**, *11*, 553–559.
[23] a) V. I. Bakhmutov, *Dihydrogen Bond: Principles, Experiments, and Applications*, Wiley-VCH, Weinheim, **2008**; b) C. P. Lau, S. M. Ng, G. Jia, Z. Lin, *Coord. Chem. Rev.* **2007**, *251*, 2223–2237; c) K. Aznavour, R. Bau, *Chemtracts* **2006**, *19*, 419–434; d) G. J. Kubas (Ed.), *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory and Reactivity*, Kluwer Academic/Plenum Publishers, Dordrecht, **2001**; e) G. R. Desiraju, *J. Chem. Soc., Dalton Trans.* **2000**, 3745–3751.
[24] H. J. Kleiner (Hoechst AG), German patent DE 92-4226554 (*Chem. Abstr.* **1994**, *120*, 270819).
[25] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

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