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# Water soluble phosphines
# Part XV. Syntheses of multiply functionalized and chiral phosphine ligands by Pd-catalyzed P–C and C–C coupling reactions☆

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**Abstract**

Phosphine ligands containing mono- and multiply substituted aromatic substituents (**1**–**13**, **19a** and **19b**) are accessible in high yields by palladium-catalyzed P–C coupling reactions between primary, secondary or disecondary phosphines and iodo- or bromoaromatic compounds. The reaction is of broad applicability and compatible with electron donor or electron acceptor substituents in *ortho*, *meta* or *para* position to the halogen in the aromatic ring systems. It may be performed in protic and aprotic solvents. The chiral spirocyclic boronato complex **15a** is formed upon reaction of **3** with boric acid, while with benzeneboronic acid **15c** with a peripheral Lewis acid group is obtained. The Pd-mediated P–C coupling reaction of primary phosphines proceeds stepwise, tailor-made chiral secondary (**16**) and tertiary phosphines (**17**) being formed in high yields. Through combination with Suzuki-type C–C coupling reactions, the scope of Pd-catalyzed P–C coupling may be extended further, novel ligands (**20a**, **20b**, **21a**, **21b**) with biphenylyl substituents being accessible. The X-ray structures of the salicylic acid derivative **3** (space group $P\bar{1}$) and of *ortho*-*iso*-propylphenyl-diphenylphosphine **6** (space group *Pbca*) have been determined. 

*Keywords:* Phosphine ligand synthesis; Pd-catalyzed P–C and C–C coupling; Consecutive reactions; Functionalized chiral phosphines; Biphenylyl substituents; X-ray structures

## 1. Introduction

Since the early work of Heck [2,3] in the 1960s, palladium-catalyzed coupling reactions have been developed as an important synthetic methodology for the carbon–heteroatom bond formation. Thus, arylamines are accessible in high yields by Pd-catalyzed C–N cross-coupling between secondary amines and arylhalides [4]. Carbon–phosphorus bond formation between phosphinates or dialkylphosphites and aromatic halides employing Pd catalysts have been reported by Xu et al. [5a,5b] and Hirao et al. [5c]. Imamoto et al. [5d,5e] employed $BH_3$-protected secondary phosphines for the synthesis of mono- and bidentate ligands by Pd-assisted P–C coupling reactions. The reactive intermediate of these reactions has been identified very recently [5f]. Due to side reactions at the P–$BH_3$ unit, these elegant coupling reactions cannot, however, be applied for the synthesis of phosphine ligands **A** bearing reactive functional groups (OH, COOH, $SO_3^-$). As shown by us before [6a], unprotected primary and secondary phosphines may be employed directly in P–C cross-coupling with functional arylhalides using a range of polar and non-polar solvents and even in aqueous two-phase systems [7].

In order to demonstrate the broad applicability of Pd-catalyzed P–C coupling reactions in ligand synthe-

☆ For Part 14 of this series see Ref. [1].

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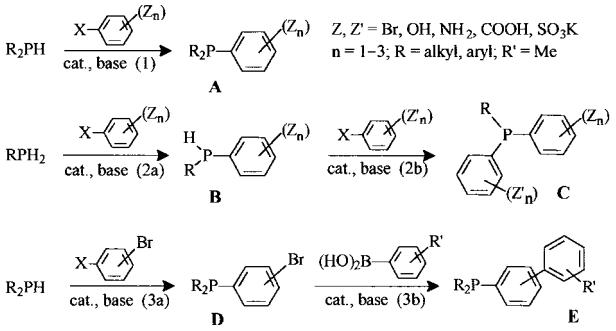
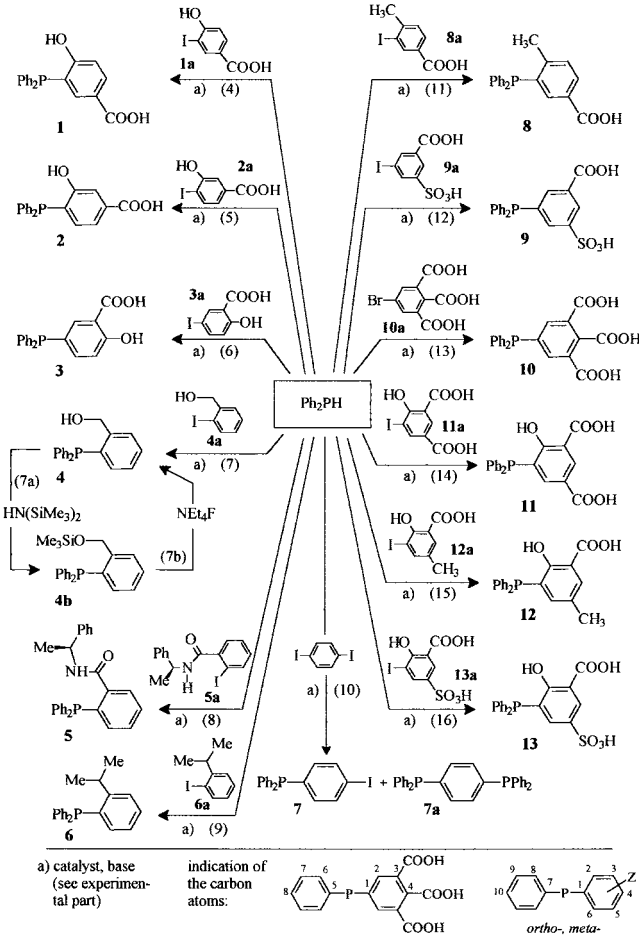
sis, we report on further examples employing polyfunctional arylhalides with substituents of variable electronic properties in different positions of the aromatic ring systems as substrates. Using primary phosphines as starting materials, consecutive replacement of the hydrogen atoms by these reactions should offer an easy access to novel chiral and multiply functionalized phosphines **B**, **C** (Eq. 2a and 2b). Part of this work has appeared in a preliminary report elsewhere [6b].

Further exploitation of this synthetic methodology may be achieved by combining Pd-catalyzed P–C and C–C cross-coupling reactions (e.g. Suzuki-type reactions) in a reaction scheme according to Eq. 3a and 3b (Scheme 1). Bromophenylphosphines, e.g. **D** [8], which are easily accessible by Pd-catalyzed P–C coupling reactions, may be employed as intermediate products (Eq. 3a) for the syntheses of bulky and chiral biphenyl-substituted phosphine ligands (**E**).




Scheme 1.




Scheme 2.

## 2. Syntheses of poly- and heterofunctional phosphine ligands

Among the various methods for the syntheses of tertiary phosphine ligands bearing functionalized aromatic substituents, nucleophilic phosphination of fluoroaromatic compounds and Pd-catalyzed cross-coupling of primary and secondary phosphines with iodoaromatic compounds are the most favorable procedures. In both cases, no introduction of protection groups at the functionalities and at phosphorus is necessary, as reported for the syntheses using Grignard [9a] or organozinc reagents [9b,9c]. While the nucleophilic phosphination reaction of fluoroaromatic compounds requires the activation of the C–F bond by electron-withdrawing substituents in *ortho* or *para* position [10], this is not a prerequisite for Pd-catalyzed P–C cross-coupling, as shown by us very recently [6].

Thus, derivatives **1**–**3** [6b] of 2- or 4-diphenylphosphinophenol with COOH substituents in *ortho*, *meta* or *para* position to the OH groups are accessible by this route using $Pd(OAc)_2$ as the catalyst (Eq. 4–6). These cross-coupling reactions may also be employed to electron-rich substrates, as shown by the synthesis of the known phosphines 2-diphenylphosphinophenol [11a,11b], 2-diphenylphosphinoaniline [11c] and 2-diphenylphosphinobenzylalcohol (**4**). They are formed under almost identical conditions as **1**–**3** in good to satisfying yields (Eq. 7, Scheme 2). For a further purification of **4**, it was transformed to its trimethylsilylether by reaction with $HN(SiMe_3)_2$, which, in contrast to **4**, could be distilled in vacuo without decomposition. Deprotection of the silylether with $NEt_4F$ yields pure **4**. This ligand was obtained in a multistage synthesis by reduction of 2-diphenylphosphinobenzoic acid or 2-(diphenylphosphino)benzaldehyde [11d,11e].

Pd-catalyzed P–C cross-coupling reactions are even compatible with peptide units, as shown by the synthesis of the chiral phosphine ligand **5** ($[\alpha]_D^{20} = +14.9°$, $c = 1.0$, $CHCl_3$) (Eq. 8). The starting material, 2-iodobenzoic acid (*R*)-(+)-phenylethylamide (**5a**), was obtained by reaction of 2-iodobenzoic acid chloride (prepared from of 2-iodobenzoic acid and $SOCl_2$) with (*R*)-(+)-1-phenylethylamine. The Pd-mediated coupling reaction is not hampered by the bulky CO–NH–CH(Me)Ph substituent. The same applies for

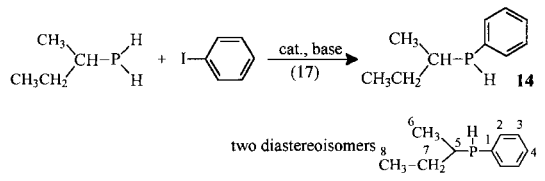
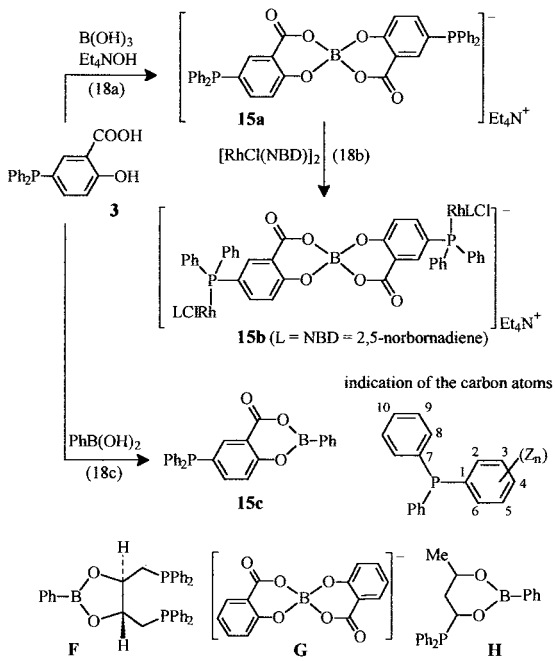



Plate 1.




Scheme 3.

the bulky *iso*-propyl group in the *ortho* position to the halogen of the aromatic ring system in **6a** during the synthesis of **6** (Eq. 9). Achiral phosphine amide ligands related to **5** have been obtained by Hedden and Roundhill [12] in moderate yield using *ortho*-(diphenylphosphino)benzoic acid as the starting material.

While Pd-assisted coupling of *ortho*-, *meta*- and *para*-bromoiodobenzene with $Ph_2PH$ gave selectively the corresponding bromophenylphosphines (see Eq. 22 below and Ref. [8]), with 1,4-diiodobenzene only a mixture of 4-iodophenyl-diphenylphosphine (**7**) and 1,4-bis(diphenylphosphino)benzene (**7a**) [11f] was obtained (Scheme 2, Eq. 10). As a reactive derivative of $Ph_3P$, the iodophenylphosphine **7** is of potential interest in ligand synthesis.

Ligands of type **1** in which the OH group is replaced by a Me substituent (e.g. **8**) may be obtained by the procedure reported here as well (Eq. 11). This method is also applicable for the high yield synthesis of phosphine ligands (**9**, **10** [6b], **11**–**13**) containing aromatic groups with two or three substituents of identical or different electronic properties (OH, COOH, $SO_3H$) (Eq. 12–16).

In summary, these results indicate that Pd-catalyzed cross-coupling reactions as developed by us are of broad applicability, the electronic nature, number and position of the substituents in the iodoaromatic substrates being of no significant influence on the yields and reaction rates by which the multiply functionalized phosphine ligands are formed (Plate 1).

The scope of this reaction may be further extended to dialkylphosphines, as shown by Hillhouse [13a] for some reactions of diisobutylphosphine with non-functionalized aromatic compounds, such as 4-bromobenzene, 4-bromotoluene and 1-bromonaphthalene. Primary alkylphosphines, like *i*-butylphosphine, may selectively be arylated with iodobenzene to yield the chiral secondary phosphine **14** (Eq. 17). Due to the presence of two centers of chirality (α-C, P), **14** is obtained as a mixture of two diastereoisomers (*erythro*–*threo*). **14** has been obtained alternatively by alkylation of $PhPH_2$ with 2-bromo-butane in the superbasic medium DMSO–KOH, $H_2O$ [13b].

Ligands **1**–**14** have been identified by their $^{31}P\{^1H\}$-, $^1H$- and $^{13}C\{^1H\}$-NMR spectra. The assignment of the signals of the aromatic carbon atoms in the $^{13}C\{^1H\}$-NMR spectra was achieved by comparison with the corresponding data of $Ph_3P$ [14] and its derivatives bearing functional groups [6a,8,10]. Further support was gained from intensity arguments, DEPT-$^{13}C$-NMR spectra and the relative magnitude of the coupling constants $^nJ_{(P-C)}$. The indication of the carbon atoms used for **1**–**14** is shown in Scheme 2.

## 3. Boric acid and benzeneboronic acid derivatives of 3

Like 2-diphenylphosphinophenol [11a], phosphines **1**, **2**, **4**, **11**–**13** are of interest as hemilabile P, O-chelating ligands [15a,15b]. Phosphine ligand **3** combines the donor properties of a $Ph_2P$ group with the chelating potential of the salicylic acid moiety [15c]. It reacts with boric acid in the presence of tetraethylammonium hydroxide to give the boric acid disalicylate complex **15a** (Eq. 18a, Scheme 3). Complex formation between salicylic acid and boric acid has been studied by Meulenhoff in the 1920s [16a,16b] and later by others in detail [16c,16d]. The complexes formed contain tetrahedral-coordinated boron in a spiro-type structure and they are stable towards dissociation. Due to the presence of a chiral boron atom [17] in **15a**, the phenyl groups of the $Ph_2P$ units are diastereotopic, two sets of resonances being observed in the $^{13}C\{^1H\}$-NMR spectrum for C7–C10 (for an indication of the carbon atoms see Scheme 3). Compounds of type **15a** represent a novel type of bidentate phosphine ligands with the donor groups kept in fixed distance by a rigid chiral spacer unit. With $[RhCl(NBD)]_2$ (NBD = bicyclo[2.2.1]hepta-2,5-diene) [18], **15a** forms a bimetallic complex **15b** (Eq. 18b)

showing a doublet at $\delta = 32.0$ due to Rh–P coupling ($J_{Rh-P} = 171.1$ Hz) in the $^{31}P\{^1H\}$-NMR spectrum. As in the free ligand, the Ph groups of the $Ph_2P$ moieties are diastereotopic, two resonances being observed in the $^{13}C\{^1H\}$-NMR spectrum for C7–C10.

On reaction of benzeneboronic acid with the phosphine ligand **3** containing a salicylic acid moiety in dichloromethane, the cyclic boronic ester **15c** is formed (Eq. 18c). The mass spectrum of **15c** shows two peaks for the molecular ion at $m/e$ 408 ($^{11}B$) and 407 ($^{10}B$) with the expected intensity ratio.

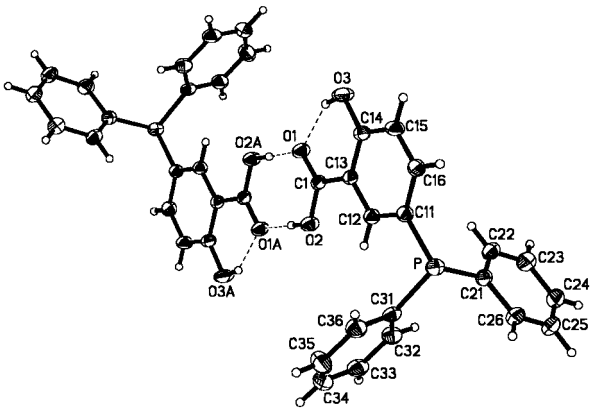



Fig. 1. Molecular structure of **3**. Selected interatomic distances (Å) and angles (°): P–C(11) 1.836(2), P–C(21) 1.832(2), P–C(31) 1.834(2), C(1)–O(1) 1.234(2), C(1)–O(2) 1.309(2), C(14)–O(3) 1.352(3), C(1)–C(13) 1.459(3), C(11)–C(12) 1.379(3), C(12)–C(13) 1.397(3), C(13)–C(14) 1.401(3), C(14)–C(15) 1.381(3), C(15)–C(16) 1.372(3), C(16)–C(11) 1.399(3), C(11)–P–C(21) 102.44(10), C(11)–P–C(31) 100.78(9), C(21)–P–C(31) 101.16(10), O(1)–C(1)–O(2) 121.98(18), O(2)–C(1)–C(13) 114.88(18), O(1)–C(1)–C(13) 123.13(18).

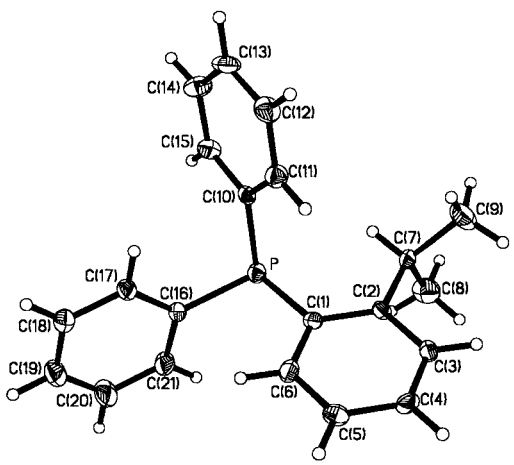



Fig. 2. Molecular structure of **6**. Selected interatomic distances (Å) and angles (°): P–C(11) 1.836(2), P–C(21) 1.832(2), P–C(31) 1.834(2), C(1)–O(1) 1.234(2), C(1)–O(2)1.309(2), C(14)–O(3) 1.352(3), C(1)–C(13) 1.459(3), C(11)–C(12) 1.379(3), C(12)–C(13) 1.397(3), C(13)–C(14) 1.401(3), C(14)–C(15) 1.381(3), C(15)–C(16) 1.372(3), C(16)–C(11) 1.399(3), C(11)–P–C(21) 102.44(10), C(11)–P–C(31) 100.78(9), C(21)–P–C(31) 101.16(10), O(1)–C(1)–O(2) 121.98(18), O(2)–C(1)–C(13) 114.88(18), O(1)–C(1)–C(13) 123.13(18).

Like the $C_2$ symmetric boron analog of DIOP (**F**) reported by Kagan et al. [19a] and Jacobsen et al. [19b], complexes of ligands of type **15c** may serve as possible templates for directing catalytic reactions by precoordination of donor-functionalized substrates. The regioselective hydroformylation of allylacetate by zwitterionic Rh complexes of 1,4-bis(diphenylphosphino)butane containing the bis[2-hydroxybenzoato(2 − )–$O^1O^2$]-borate ( − 1) anion (**G**) yields the linear aldehyde in a 93:7 selectivity [20]. Phosphine ligands (**H**) containing the 1,3,2-dioxaborinane skeleton have been recently reported by Balueva et al. [21].

## 4. X-ray structure of 3 and 6

By recrystallization of **3** from $CH_2Cl_2$ crystals of composition $C_{19}H_{15}O_3P$ suitable for X-ray structural analysis could be obtained. The results are shown in Fig. 1, selected bond lengths and bond angles are given in the caption to Fig. 1.

In the solid state, the molecules of **3** are arranged in columns that are interconnected by hydrogen bridging between the COOH substituents. As in salicylic acid [22a], the OH groups of **3** are engaged in intramolecular hydrogen bonds building a very common motive of intramolecular hydrogen bridging [22c].

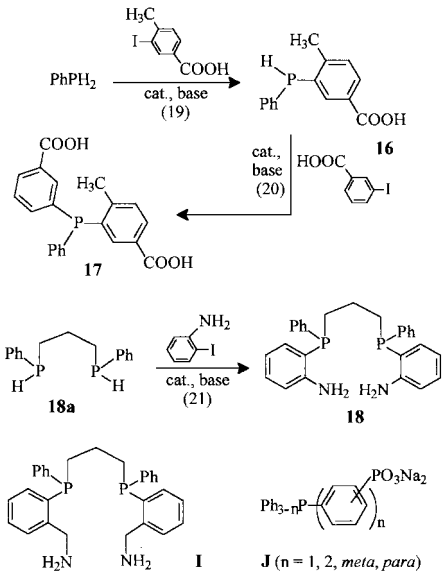
The hydrogen bridging motive found in the solid state of **3** is typical for carboxylic acids [22b,22d], and different C–O bond lengths are observed (e.g. 1.25 and 1.36 Å in HCOOH dimers) [23]. In **3**, the carbon–oxygen distances are C(1)–O(1) = 1.234(2) Å and C(1)–O(2) = 1.309(2) Å, the O(1)–C(1)–O(2) bond angle being 121.98(18)°. The P–C bond lengths and C–P–C bond angles do not differ significantly from the corresponding values found for $Ph_3P$ [24], the phenyl groups are orientated in a propeller-type arrangement (dihedral angles C(11)–P–C(31)–C(36) = − 94.86(19)°, C(31)–P–C(21)–C(26) = − 77.08(19)°, C(21)–P–C(11)–C(16) = − 97.76(19)°). The oxygen atoms O(1) and O(2) of the COOH substituent are almost coplanar with the aromatic ring system C(11)–C(16). As a consequence of the interaction between O(3) and O(1), the bond length C(14)–O(3) is 1.352(3) Å and the bond angles C(13)–C(1)–O(1) and C(13)–C(14)–O(3) are widened up to 123.13(18) or 122.75(20)°, respectively.

Crystals of **6** suitable for X-ray structural analysis could be obtained by recrystallization from ethanol. The results are shown in Fig. 2 with selected bond lengths and bond angles given in the caption. As in **3**, the P–C bond lengths and P–C–P bond angles may be compared well with the corresponding values found for $Ph_3P$ [24]. The *i*-Pr substituent in the *ortho* position does not significantly influence the geometry of the $PC_3$ skeleton. The planes defined by the aromatic carbon atoms of each aryl ring are rotated in the same sense

against the phosphorus substituent plane defined by the atoms C(1), C(10) and C(16). Furthermore, the angle formed by the isopropyl substituted ring (48.9(2)°) lies between the values found for the two phenyl groups (44.6(1) and 51.6(1)°). The isopropyl group is located on the phosphorus side of its above-mentioned substituent plane. This orientation directs the bulky substituent away from the pseudo-threefold axis of the molecule and thus reduces the steric congestion between the groups bonded to the phosphorus atom. This seems to be the preferred conformation of the $C_6H_4$–2-*i*-Pr group with respect to the P–C(1) rotational axis also in solution as indicated by the large coupling constant $^2J_{(P-C)}$ (23.4 Hz) observed for *ortho*-carbon atom bearing an isopropyl substituent (C(2)) in the $^{13}C\{^1H\}$-NMR spectrum of **6**. In general, $^2J_{(P-C)}$ is large when the lone pair is close to the C atom, and it is small when remote [25–27]. The latter applies for the unsubstituted *ortho*-carbon atom C(6), for which no P–C coupling fine structure was observed in the $^{13}C\{^1H\}$-NMR spectrum.

## 5. Syntheses of functionalized chiral secondary and *tertiary* phosphine ligands by consecutive Pd-catalyzed P–C coupling reactions

Pd-catalyzed P–C coupling reactions of primary phosphines, e.g. $PhPH_2$, with arylhalides in a 1:2 stoichiometry afford highly functionalized tertiary phosphines, secondary phosphines being formed in a consecutive reaction as intermediates [6,7]. If, however, equimolar amounts of the reactants are employed, functionalized chiral secondary phosphine ligands, e.g. **16**, may selectively be obtained in high yields (Eq. 19).




Scheme 4.

A mixture of tris(dibenzylideneacetone) dipalladium chloroform adducts and 1,3-bis(phenylphosphino)-propane in a 1:1 molar ratio was used as the catalyst. In their synthesis of secondary phosphines, Beletskaya et al. [5g] used the elusive silylphosphines $RP(H)SiMe_3$ in a Stille-type coupling reaction. This method suffers from the reactivity of the P–Si bond towards polar substituents such as OH, $NH_2$, COOH in the substrate molecules. By standard methods, these multifunctional ligands are accessible only in low yield multistage syntheses using protective groups. Functionalized secondary phosphines are valuable starting materials for the syntheses of chiral tertiary phosphine ligands as exemplified by the successful preparation of **17** by consecutive Pd-catalyzed P–C coupling reactions. Ligands of type **16** and **17** are of great potential in parallel syntheses [28a] and combinatorial catalysis [28b].

Ligand tailoring by Pd-catalyzed P–C coupling reactions can also be achieved using disecondary phosphines as starting materials. Thus, the $P_2N_2$ hybrid ligand **18** [29] with *ortho*-aminophenyl substituents was obtained in high yield by coupling 1,2-diphenylphosphinopropane (accessible by standard techniques) with *ortho*-iodoaniline using $Pd(OAc)_2$ as the catalyst (Eq. 21). The bidentate ligands (**18** and **18a**) obviously do not deactivate the catalyst system by formation of stable Pd(0) chelate complexes in this reaction. **18** was obtained as a 1:1 mixture of two diastereoisomers I ($\delta = -34.2$) and II ($\delta = -34.3$). On recrystallization from methanol, an enrichment of diastereoisomer I in a 8:3 ratio was achieved. In the $^{13}C\{^1H\}$-NMR spectrum, the two diastereoisomers show first-order triplets for the center carbon atom of the $CH_2$–$CH_2$–$CH_2$ bridge, while overlapping higher-order pattern (X part of a ABX spectra; X = $^{13}C$; A, B = $^{31}P$) are observed for all other carbon atoms with exeption of those in *para*-position to phosphorus within the aromatic ring systems for which only singlets are obtained.

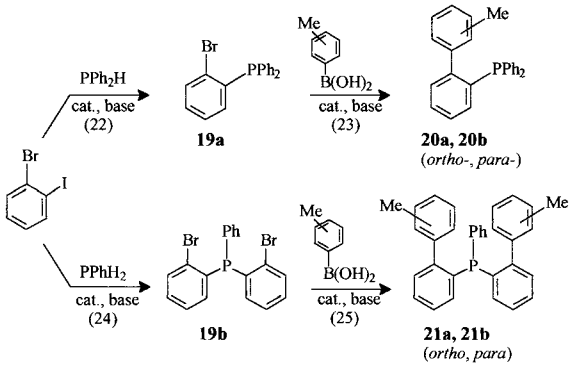
The $P_2N_2$ hybrid ligand **I** related to **18** has been synthesized very recently by us using nucleophilic phosphination reaction using 2-phenylphosphino benzylamine as starting material (Scheme 4) [1].

## 6. Synthesis of phosphine ligands by combination of Pd-catalyzed P–C and C–C coupling reactions

As shown for the chiral ligand **17** in this paper (Eq. 19 and 20) and for the phosphonato phosphines **J** [8] reported earlier by us, consecutive Pd-catalyzed P–C coupling reactions may be used for a systematic tailoring of phosphine ligands. Combination of P–C and C–C cross-coupling reactions should extend the scope of metal-mediated ligand synthesis considerable.

Since the work reported here was also directed towards the syntheses of aromatic phosphines bearing

aryl substituents in *ortho*-position to phosphorus, we have chosen the bromophenylphosphines **19a** [30] and **19b** as starting materials (Scheme 5). They are easily accessible in high yields by Pd-catalyzed P–C coupling between *ortho*-bromoiodobenzene with phenyl- or diphenylphosphine. $Pd(Ph_3P)_4$ was employed as the catalyst in this reaction (Eq. 22 and 24). Introduction of the aryl substituents was achieved by Suzuki-type reactions [31] with *ortho*- or *para*-tolylboronic acid (Eq. 23 and 25). The ligands **20a**, **20b** and **21a**, **21b** containing 2-biphenylyl substituents are formed in low to satisfying yields. While **20a**, **20b** ($\delta = -11.7, -12.3$) and **21b** ($\delta = -18.8$) show only one signal in the $^{31}P\{^1H\}$-NMR spectrum, three resonances are observed for **21a** ($\delta = -17.1, -20.1, -20.2$), indicating the presence of three diastereoisomers (one racemate and two *meso*-forms) for **21a** with two axially chiral biphenylyl substituents as shown schematically in Fig. 3. This interpretation is supported by the observation of four $^{13}C\{^1H\}$-NMR resonances for the *ortho*-methyl groups of the tolyl substituents. Two of them may be assigned to the *meso*-forms I and II with equivalent *ortho*-methyl groups. In case of the racemate the *ortho*-methyl groups or the *ipso*-carbon atoms are inequivalent. A similar situation is met with the disecondary butylphosphine $(secBu)_2PH$ with two centers of asymmetry at the α-carbon atoms. As in the case of **21a** three resonances are observed in the $^{31}P\{^1H\}$-NMR spectrum [32].




Scheme 5.

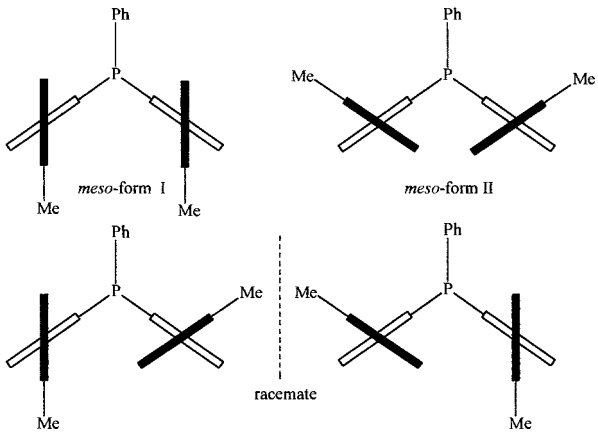



Fig. 3. Diastereoisomers of **21a**.

The mass spectrum of **21a** shows the $M^+$ peak at $m/e$ at 442 (63%), the basis peak corresponding to the fragment ion $M^+–CH_3–H$ ($m/e = 426$).

Due to the presence of an element of axial chirality the two phenyl groups of the $PPh_2$ substituent in **20a** are chemically non-equivalent. As a result of partial overlap of the 20 signals to be expected for the aromatic carbon atoms, only 19 are observed in the $^{13}C\{^1H\}$-NMR spectrum of **20a**. In the *para*-isomer **20b**, however, the Ph groups of the $PPh_2$ substituent are enantiotopic. Therefore, only a total of 14 resonances appears in the $^{13}C\{^1H\}$-NMR spectrum for the aromatic carbon atoms.

Phosphines of type **21a** with two axially chiral substituents have to the best of our knowledge not been reported in the literature before. They are of interest as starting materials for the syntheses of chiral bulky water-soluble phosphines by direct sulfonation with oleum [33].

## 7. Experimental

For experimental details, see part 14 of this series [1]. Phenylphosphine, diphenylphosphine [34a,34b], 1,3-bis(phenylphosphino)propane [34c,34d] and $Pd(Ph_3P)_4$ [34e] were synthesized by known methods. The iodo compounds **3a**, **4a**, **6a** and **8a** were purchased from Aldrich GmbH, Fluka and Lancaster Syntheses, while **1a**, **2a**, **9a** and **13a** have been obtained in a Sandmeyer-type reaction using the corresponding commercially available anilines as starting materials [35]. 5-Amino-3-sulfobenzoic acid and 3-amino-2-hydroxy-5-sulfobenzoic acid for the syntheses of **9a** and **13**a have been donated by the Bayer AG. 2-Butylphosphine was a gift of Clariant GmbH. Bromohemimellitic acid **10a** was prepared according to the literature procedure [36]. **11a** and **12a** were synthesized by direct iodination of 4-hydroxyisophthalic acid or 2-hydroxy-5-methyl benzoic acid, respectively, with iodine/silver sulfate [37]. Tris-(dibenzylideneacetone) dipalladium chloroform adduct, benzene boronic acid, o*rtho*- and *para*-toluene boronic acid have been purchased from Aldrich GmbH. The starting materials were characterized by $^1H$-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy and mass spectrometry. $^1H$-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC 400 or AM 250 and a JEOL FX90 Q Fourier transform spectrometer, mass spectra were obtained on a Varian MAT 311A.

Table 1
Synthesis of **1**–**3**, **8**, **11**, **12**

| | Iodo compounds (g (mmol)) | $Ph_2PH$ (g (mmol)) | $NEt_3$ (g (mmol)) | $CH_3CN$ (ml) | $Pd(OAc)_2$ (mg (μmol)) | Reaction conditions | KOH ((1n) ml) | Yield (g (%)) |
|---|---|---|---|---|---|---|---|---|
| **1** | 1.32 (5) **1a** | 0.93 (5) | 1.02 (10) | 10 | 1.1 (5) | 48 h, 90 °C | 10 | 0.8 (49) |
| **2** | 13.2 (50) **2a** | 9.31 (50) | 10.2 (100) | 100 | 5.6 (25) | 18 h, 100 °C | 100 | 10.6 (66) |
| **3** | 2.08 (7.9) **3a** | 1.47 (7.9) | 1.6 (16) | 30 | 2.0 (9) | 12 h, 85 °C | 16 | 1.7 (67) |
| **8** | 9.85 (37.6) **8a** | 7.0 (37.6) | 8.1 (80) | 90 | 8.5 (38) | 18 h, 90 °C | 80 | 7.3 (61) |
| **11** | 11.6 (37.7) **11a** | 7.0 (37.7) | 12.1 (120) | 90 | 8.5 (38) | 40 h, 85 °C | 120 | 9.4 (68) |
| **12** | 27.8 (100) **12a** | 18.6 (100) | 20.2 (200) | 250 | 22.5 (100) | 48 h, 90 °C | 120 | 22.2 (66) |

### *7.1. General procedure for the syntheses of **1**–**3**, **8**, **11**, **12***

The iodoaromatic compounds, diphenylphosphine, triethylamine and the corresponding amounts of the catalyst $Pd(OAc)_2$ were dissolved in acetonitrile. The amounts of the reactants are collected in Table 1. Traces of oxygen dissolved in the solutions were removed by three freeze–thaw cycles using purified nitrogen as inert gas. The reaction mixtures were then heated to 85–100 °C for several hours. Completion of the reactions was checked by $^{31}P\{^1H\}$-NMR spectroscopy. After cooling, the reaction mixtures to ambient temperature all volatiles were removed in vacuo (30 °C, 1 mbar). The residues were dissolved in 1 N KOH and the solutions were washed with two aliquots of diethylether and petrolether (40/60). The aqueous solution was cooled to 5 °C, and 2 N HCl was added until a pH value of 2 was reached. The precipitate formed was filtered off, dissolved in diethylether and the solution was dried over magnesium sulfate. The residue obtained after evaporation of the solvent in vacuo (30 °C, 1 mbar) was recrystallized from $CH_2Cl_2$ or ethanol–water mixtures. Yields are given in Table 1.

**1**, Anal. Found: C, 69.34; H, 4.84. $C_{19}H_{15}O_3P\cdot 0.5H_2O$ (331.3). Calc.: C, 68.88; H, 4.87%. MS: *m*/*e* 322 [$M^+$]. $^1$H-NMR ($d_6$-DMSO, $\delta$): 12.4 (COOH), 10.6 (OH), 7.6–7.2 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 123.2 (14.2), 163.2 (16.2), 114.6, 132.2, 121.9, 135.0, 136.1 (12.1), 133.4 (20.2), 128.6 (7.1), 128.8, 166.9 (COOH); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −15.5.

**2**, Anal. Found: C, 68.68; H, 4.96. $C_{19}H_{15}O_3P\cdot 0.5H_2O$ (331.3). Calc.: C, 68.88; H, 4.87%. MS: *m*/*e* 322 [$M^+$]. $^1$H-NMR ($d_6$-DMSO, δ): 10.2 (COOH), 4.0 (OH), 7.6–7.2 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 129.5 (15.1), 159.6 (15.2), 115.6 (6.1), 133.2, 120.8, 133.3, 136.5 (11.1), 134.1 (20.2), 129.2 (7.1), 129.5, 167.8 (COOH); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −14.9.

**3**, Anal. Found: C, 70.91; H, 4.89. $C_{19}H_{15}O_3P$ (322.3). Calc.: C, 70.81; H 4.69%. MS: *m*/*e* 322 [$M^+$]. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 10.6 (COOH), 8.1–7.0 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 126.6 (10.1), 136.6 (24.3), 118.6 (6.1), 162.6, 114.4 (9.1), 141.0 (19.2), 137.5 (11.1), 133.6 (19.2), 129.3 (6.1), 129.5, 172.0 (COOH); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −6.6.

**8**, Anal. Found: C, 74.63; H, 5.50. $C_{20}H_{17}O_2P$ (320.3). Calc.: C, 74.99; H, 5.35%. MS: *m*/*e* 320 [$M^+$]. $^1$H-NMR ($d_6$-DMSO, $\delta$): 11.6 (COOH), 2.3 ($CH_3$), 7.1–8.0 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 136.4 (14.1), 146.6 (25.3), 129.8, 133.0, 128.7, 130.5 (4.1), 135.0 (10.2), 133.6 (19.9), 129.0 (7.1), 129.3, 167.0 (COOH), 20.9 (20.4, $CH_3$); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −11.1.

**11**, Anal. Found: C, 65.81; H, 4.27. $C_{20}H_{15}O_5P\cdot$ (366.3). Calc.: C, 65.58; H, 4.13%. MS: *m*/*e* 366 [$M^+$]. $^1$H-NMR ($d_6$-DMSO, $\delta$): 7.1–8.5 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 126.4 (7.2), 166.5 (16.7), 112.6, 133.6, 122.5, 140.1, 135.7 (11.1), 134.0 (20.2), 129.1 (7.1), 129.4, 166.6 (COOH), 172.4 (COOH); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −15.8.

**12**, Anal. Found: C, 69.73; H, 5.33. $C_{20}H_{17}O_3P\cdot 0.5H_2O$ (345.3). Calc.: C, 69.57; H, 5.24%. MS: *m*/*e* 336.6 [$M^+$]. $^1$H-NMR ($d_6$-DMSO, $\delta$): 10.2 (COOH), 2.2 ($CH_3$), 6.8–7.9 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 126.0 (15.2), 161. 5 (16.2), 110.5 (2.8), 131.5, 141.6, 136.6 (9.1), 133.8 (20.2), 128.5 (7.1), 128.9, 174.9 (1.5, COOH), 20.4 ($CH_3$); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −15.6.

### *7.2. Synthesis of **4***

5.34 g (28.7 mmol) of diphenylphosphine and 6.72 g (28.7 mmol) of 2-iodobenzyl alcohol were dissolved in 40 ml of *N*,*N*-dimethylacetamide. To this solution, 2.94 g (30.0 mmol) of KOAc and 2.9 ml of a $Pd(OAc)_2$ stock solution in *N*,*N*-dimethylacetamide (10 μmol $ml^{-1}$) were added. The reaction mixture was heated to 130 °C for 12 h. Thereafter, it was poured onto an ice–water mixture and extracted with three aliquots of 10 ml of $CH_2Cl_2$. The organic phase was separated, washed with two portions of 20 ml of water and dried over $Na_2SO_4$. After removal of the solvent in vacuo, **4** was obtained as a yellow solid. The solid obtained above was treated with excess $HN(SiMe_3)_2$ (2.4 g, 14.9 mmol) and a small

amount of $CF_3COOH$ (0.1 g). This mixture was heated to 150 °C for 10 min. All volatiles were removed in vacuo. Short path distillation of the residue in vacuo (200–250 °C, 0.001 mbar) yielded the *O*-trimethylsilylether **4b** of **4** as a colorless off-white solid. Yield: 9.5 g (91%). It was identified by $^1$H-, $^{31}$P{$^1$H}-, $^{13}$C{$^1$H}- and $^{29}$Si-NMR spectroscopy. For deprotection, **4b** was dissolved in 30 ml of THF and treated with 4.47 g (30.0 mmol) of $NEt_4F$ at ambient temperature for 30 min. After reducing the volume of the reaction mixture in vacuo to ca. 10 ml, 100 ml of water was added. The precipitate formed was extracted with three aliquots of 20 ml of $CH_2Cl_2$. The organic extracts were washed with water and dried over $Na_2SO_4$. After evaporation of the solvent, the remaining residue was dried in vacuo (50 °C, 0.01 mbar). **4** was obtained as a viscous colorless oil. Yield: 8.3 g (99%).

**4**, Anal. Found: C, 77.74; H, 5.94. $C_{19}H_{17}OP$ (292.3). Calc.: C, 78.07; H, 5.86%. $^1$H-NMR ($CDCl_3$, $\delta$): 4.86 (1.3, $CH_2$), 2.81 (OH), 6.9–7.8 (arom. H); $^{13}$C{$^1$H}-NMR ($CDCl_3$, $\delta$): (C1–C10) 134.6 (14.0), 144.8 (23.0), 127.7 (5.9), 129.1, 127.6 (1.2), 133.2, 135.9 (9.0), 133.8 (19.6), 128.5 (7.1), 128.6, 63.4 (23.1, $CH_2$); $^{31}$P{$^1$H}-NMR ($CDCl_3$, $\delta$): −15.0.

**4b**, $C_{22}H_{25}OPSi$ (364.5): $^1$H-NMR ($CDCl_3$, $\delta$): 0.11 ($CH_3$), 4.93 ($CH_2$), 6.9–7.7 (arom. H); $^{13}$C{$^1$H}-NMR ($CDCl_3$, $\delta$): (C1–C10) 133.8, 145.1 (22.2), 126.5 (5.7), 128.9, 127.1 (0.9), 133.0, 136.3 (9.6), 133.8 (19.7), 128.5 (7.0), 128.7, 62.8 (26.8, $CH_2$), −0.6 (58.8, $^1J_{(C-Si)}$, $SiMe_3$); $^{31}$P{$^1$H}-NMR ($CDCl_3$, $\delta$): −15.1; $^{29}$Si{$^1$H}-NMR ($CDCl_3$, $\delta$): 19.6.

### 7.3. Synthesis of **5**

2-Iodobenzoyl chloride was prepared by reaction of 12.4 g (50 mmol) of 2-iodobenzoic acid with 60 ml of $SOCl_2$. It was dissolved in 30 ml of $CH_2Cl_2$ and this solution was treated with 6.1 g (50 mmol) of (*R*)-(+)-1-phenylethylamine. Thereafter all volatiles were evaporated in vacuo leaving **5a** as a white solid. Yield: 16.2 g (92%). **5a** was identified by its $^1$H- and $^{13}$C{$^1$H}-NMR spectrum; $[\alpha]_D^{20} = +29°$, $c = 10$, ethanol. A solution of 5.54 g (28.7 mmol) of $Ph_2PH$ in 80 ml of *N*,*N*-dimethylacetamide was charged with 10.08 g (28.7 mmol) of **5a** and 2.9 ml of $Pd(OAc)_2$ stock solution in *N*,*N*-dimethylacetamide (10 μmol ml$^{-1}$). After heating the reaction mixture to 100 °C for 12 h it was poured into 500 ml of water and the solid formed was extracted with 60 ml of $CH_2Cl_2$. For the removal of traces of the Pd catalyst, the organic phase was extracted with three aliquots of 5 ml of conc. aqueous solution of KCN. After washing with water the organic phase was dried over $Na_2SO_4$. The residue remained after removal of the solvent in vacuo was recrystallized from methanol. **5** was obtained as colorless needles. Yield: 10.5 g (89%).

**5**, Anal. Found: C, 79.09; H, 5.92; N, 3.39. $C_{27}H_{24}NOP$ (409.5). Calc.: C, 79.20; H, 5.91; N, 3.42%. $^1$H-NMR ($CDCl_3$, $\delta$): 1.38 (6.9, $CH_3$), 5.17 (CH), 6.46 (6.9), 6.9–7.7 (arom. H); $^{13}$C{$^1$H}-NMR ($CDCl_3$, δ): (C1–C10) 135.0 (19.6), 141.3 (26.0), 128.0 (5.1), 130.0, 128.8, 133.9, 136.7 (10.3), 136.4 (10.2), 133.8 (18.7), 133.6 (20.0), 128.6 (8.2), 128.4 (7.9), 128.7, 167.9 (0.8, CO), 49.4 (CH), 21.3 ($CH_3$) 142.6 (Ph), 128.4 (Ph), 126.1 (Ph), 127.0 (Ph); $^{31}$P{$^1$H}-NMR ($CDCl_3$, $\delta$): −9.4.

**5a**, $^1$H-NMR ($CDCl_3$, δ): 1.61 (6.9, $CH_3$), 5.29 (CH), 6.21 (6.9, NH), 6.9–7.9 (arom. H); $^{13}$C{$^1$H}-NMR ($CDCl_3$, $\delta$): (C1–C10) 92.4, 142.1, 128.3, 127.5, 131.0, 139.7, 142.5, 126.4, 128.6, 128.1, 168.4 (CO), 49.4 (CH), 21.4 ($CH_3$).

### 7.4. Synthesis of **6**

10.0 g (41.0 mmol) of 2-iodo-isopropylbenzene, 7.63 g (41.0 mmol) of $Ph_2PH$, 4.55 g (45.0 mmol) of $NEt_3$ and 0.47 g (1 mol%) of $Pd(Ph_3P)_4$ were dissolved in 60 ml of toluene. The reaction mixture was heated for 24 h at 80 °C, during this time the color of the reaction mixture changed from yellow to violet. The residue obtained after evaporation of the solvent was dissolved in 100 ml of dichloromethane and washed with two aliquots of a 1 M aqueous KCN solution. The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The remaining solid was recrystallized from an ethanol–water mixture. Yield: 9.95 g (80%).

**6**, Anal. Found: C, 82.60; H, 6.93. $C_{21}H_{21}P$ (304.4). Calc.: C, 82.86; H, 6.97%. MS: *m*/*e* 304 [M$^+$]. $^1$H-NMR ($CDCl_3$, $\delta$): 1.9 (6.6, $CH_3$), 3.8 (CH), 6.9–7.4 (arom. H); $^{13}$C{$^1$H}-NMR ($CDCl_3$, $\delta$): (C1–C10) 134.3 (9.2), 153.4 (23.4), 126.0, 129.3, 125.5 (5.1), 133.4, 137.1 (10.2), 134.0 (19.3), 128.5 (7.1), 128.6, 31.3 (25.4, CH), 23.9 ($CH_3$); $^{31}$P{$^1$H}-NMR ($CDCl_3$, $\delta$): −13.9.

### 7.5. Synthesis of **7** and **7a**

13.2 g (71.0 mmol) of diphenylphosphine and 7.64 g (78.0 mmol) of KOAc were added to a solution of 23.4 g (71.0 mmol) of 1,4-diodobenzene in 120 ml of dimethylacetamide. After addition of 7.1 ml of a stock solution of $Pd(OAc)_2$ (10 μmol ml$^{-1}$) the reaction mixture was heated to 70–80 °C. Thereafter 150 ml of water was added and the solution was extracted with 150 ml of dichloromethane. The organic phase was dried over $MgSO_4$. All volatiles were removed in vacuo leaving a colorless solid containing **7** and **7a** in about equal amounts. They were separated by fractional crystallization from ethanol–water. Yields: 12.4 g (45%) **7**; 11.8 g (45%) **7a**.

**7**, Anal. Calc. for $C_{18}H_{14}IP$ (388.2): C, 55.70; H, 3.64. Found: C, 56.02; H, 3.69%. MS: *m*/*z* (%) 388 [M$^+$]. $^1$H-NMR ($C_6D_6$, $\delta$): 6.88–7.44 (arom. H); $^{13}$C{$^1$H}-

NMR ($C_6D_6$, $\delta$): (C1–C8) 137.7, 135.4 (19.3), 137.6 (7.1), 95.3, 136.9 (11.2), 133.8 (20.4), 128.7 (6.1), 128.9; $^{31}P\{^1H\}$-NMR ($C_6D_6$, $\delta$): −4.8.

### 7.6. Synthesis of **9**

7.00 g (37.6 mmol) of diphenylphosphine and 12.34 g (37.6 mmol) of **9a** were dissolved in a mixture of 100 ml of acetonitrile and 10 ml of *N*,*N*-dimethylacetamide. After addition of 12.14 g (120.0 mmol) of triethylamine and 1.0 g (5.4 mmol) of tributylamine 8.4 mg (37.6 μmol) of palladium(II) acetate was added. Traces of oxygen dissolved in the solutions were removed by three freeze–thaw cycles using purified nitrogen as inert gas. The reaction mixture was heated for 36 h to 95 °C. Thereafter all volatiles were removed in vacuo (80 °C, 0.1 mbar) and the remaining residue was dissolved in 120 ml of 1 N sodium hydroxide. The solution obtained was washed with five aliquots of 30 ml of diethylether and 30 ml of *n*-hexane. After addition of 10 ml of 2 N HCl, the solution was heated to 100 °C. On cooling to ambient temperature, **9** was precipitated from the solution as white needles which were dried in vacuo (100 °C, 0.1 mbar). Yield: 11.1 g (76%).

**9**, Anal. Found: C, 58.73; H, 4.22. $C_{19}H_{15}O_5PS$ (386.3). Calc.: C, 59.07; H 3.91%. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.1–7.7 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 137.7 (15.2), 134.0 (22.2), 131.0 (6.1), 127.2, 148.7 (6.1), 133.6 (20.2), 135.8 (11.2), 133.4 (20.2), 129.0 (7.1), 129.4, 166.6 (COOH); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −4.8.

### 7.7. Synthesis of **10**

To a solution of 5.78 g (20.0 mmol) of **10a** and 3.72 g (20.0 mmol) of $Ph_2PH$ in 45 ml of *N*,*N*-dimethylacetamide 15.76 g (85.0 mmol) of $n$Bu$_3$N and 9.0 mg (40 μmol) of $Pd(OAc)_2$ were added under a blanket of nitrogen. The reaction mixture was heated to 130–140 °C for 48 h. Thereafter, the volume of the reaction mixture was reduced to about 25 ml by evaporation in vacuo (100 °C, 0.1 mbar). After cooling to room temperature, a solution of 3.20 g (80.0 mmol) of NaOH in 60 ml of water was added, a two-phase system being formed. The upper phase was discarded, the lower phase was extracted with three aliquots of 25 ml of *n*-hexane. On addition of 120 ml of a 0.6 N HCl, a precipitate was formed which redissolved on heating the mixture to 100 °C. Cooling down again to ambient temperature **10** was precipitated as colorless white needles. Yield: 6.23 g (79%).

**10**, Anal. Found: C, 63.49; H 4.24. $C_{21}H_{15}O_6P$ (394.3). Calc.: C, 63.97; H 3.83%. MS: $m/e$ 376 [$M^+$ –$H_2O$]. $^1$H-NMR ($d_6$-DMSO, $\delta$): 13.3 (COOH), 7.2–7.9 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C8) 139.1 (16.2), 136.7 (19.2), 130.2 (5.1), 136.6, 135.1 (11.1), 133.5 (20.2), 129.1 (7.1), 129.6, 168.6 (1.1, COOH), 166.7 (COOH); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, δ): −5.6.

### 7.8. Synthesis of **13**

To a solution of 9.26 g (26.9 mmol) of **13a** and 14.96 g (80.7 mmol) of $n$Bu$_3$N in 45 ml of *N*,*N*-dimethylacetamide 5.0 g (26.9 mmol) of $Ph_2PH$ and 6.0 mg (27 μmol) of palladium(II) acetate were added. Traces of oxygen dissolved in the solution were removed by three freeze–thaw cycles using purified nitrogen as inert gas. The mixture was heated to 135 °C for 16 h. Thereafter, all volatiles were removed in vacuo (100 °C, 0.1 mbar). To the remaining residue 50 ml of a 1.6 N NaOH was added. The upper organic phase of the two-phase system was discarded, the aqueous phase was evaporated to dryness in vacuo (30 °C, 0.1 mbar). The residue obtained was extracted with three aliquots of boiling acetone and two aliquots of 25 ml of ethanol and then dissolved in 30 ml of water. On acidification of the aqueous solution, **13** was precipitated as a faint yellow solid. Yield: 5.88 g (54%).

**13**, Anal. Found: C, 55.84; H, 4.18. $C_{19}H_{15}O_6PS\cdot 0.5H_2O$ (411.4). Calc.: C, 55.48; H 3.92%. $^1$H-NMR ($D_2O$, $\delta$): 7.0–8.0 (arom. H); $^{13}C\{^1H\}$-NMR ($D_2O$, $\delta$): (C1–C10) 125.2 (14.2), 163.6 (15.2), 111.5 (3.0), 128.8 (3.0), 135.7, 135.8, 134.0 (6.1), 133.3 (20.2), 128.5 (7.1), 129.2, 171.3 (COOH); $^{31}P\{^1H\}$-NMR ($D_2O$, $\delta$): −12.3.

### 7.9. Synthesis of **14**

3.96 g (44.2 mmol) of 2-butylphosphine, 9.01 g (44.2 mmol) of iodobenzene and 5.06 g (50.0 mmol) of triethylamine were dissolved in 30 ml of dimethylacetamide. After addition of 0.414 g of *trans*-di(μ-acetato)-bis[*ortho*-(di-2-tolylphosphino)benzyl]dipalladium(II) [38] the reaction mixture was heated for 12 h to 100 °C. After cooling down to ambient temperature 100 ml of water were added and the reaction mixture was extracted with 50 ml of *n*-pentane. The organic phase was separated and washed with three aliquots of 10 ml of water and dried with $Na_2SO_4$. Thereafter, the solvent was removed in vacuo and the remaining product was condensed at 60 °C, 0.001 mbar into a flask chilled with dry ice. Yield: 5.4 g (74%). The colorless malodorous product was identified by NMR spectroscopy.

**14**, $^1$H-NMR ($CDCl_3$, $\delta$): 0.85 (7.4, $CH_3$), 0.86 (7.4, $CH_3$), 0.95 (14.8, 6.9, $CH_3$), 1.01 (11.4, 7.1, $CH_3$), ca. 1.24 (m, $CH_2$), ca. 1.48 (m, $CH_2$), ca. 1.70 (m, CH), ca. 1.78 (m, CH), 3.94 (205.5, 6.4, PH), 4.10 (205.5, 5.3, PH), 7.0–7.5 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1, C1′–C8, C8′) 134.3 (13.2), 133.9 (13.2), 134.2 (15.5), 133.8 (15.1), 127.9 (5.4), 127.9 (5.9), 127.9, 127.8, 30.8 (10.0), 30.3 (9.1), 18.8 (5.9), 17.7 (15.5), 28.0 (9.9),

27.6 (15.3), 11.9 (8.1), 11.8 (11.3); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −20.5, −24.8 ($^1J_{(P-H)} = 205.5$).

### 7.10. Synthesis of **15a**

0.31 g (5.0 mmol) of boric acid dissolved in 5 ml of water were added to a solution of 3.22 g (10.0 mmol) of **3** in 20 ml of ethanol. After addition of 2.10 g (15.0 mmol) of a 35% aqueous solution of $NEt_4OH$ the reaction mixture was heated to 80 °C for 1 h. The residue obtained after removal of all volatiles in vacuo (30 °C, 1 mbar) was recrystallized from a 2-propanol–*N*,*N*-dimethylacetamide 50:20-mixture. Yield: 2.56 g (66%).

**15a**, Anal. Found: C, 70.21; H, 6.32; N, 1.77. $C_{46}H_{46}BNO_6P_2$ (781.6). Calc.: C, 70.69; H, 5.93; N 1.79%. $^1H$-NMR ($CDCl_3$, $\delta$): 3.1 ($CH_2$), 1.11 (7.2, $CH_3$), 6.8–8.2 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 125.5 (9.1), 135.0 (22.2), 118.9 (8.1), 159.8, 115.5 (8.1), 139.8 (21.2), 137.59 (12.1), 137.61 (12.1), 133.18 (19.2), 133.22 (19.2), 128.39 (7.1), 128.41 (7.1) 128.49, 128.51, 163.0 (CO), 52.2 ($CH_2$), 7.1 ($CH_3$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): −6.5.

### 7.11. Synthesis of **15b**

0.39 g (0.5 mmol) of **15a** dissolved in 10 ml of $CH_2Cl_2$ were added to a solution of 0.23 g (0.5 mmol) of [Rh(norbornadiene)Cl]$_2$ in 10 ml of $CH_2Cl_2$. The reaction mixture was stirred at ambient temperature for 2 days. After evaporation of the solvent in vacuo (20 °C, 0.1 mbar) **15b** was left as brown solid. Yield: 0.62 g (100%).

**15b**, Anal.. Found: C, 57.49; H, 5.24. $C_{60}H_{62}BCl_2NO_6P_2Rh_2$ (1242.6). Calc.: C, 57.99, H, 5.03%. $^1H$-NMR ($CDCl_3$, $\delta$): 7.6–7.2 (arom. H); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): = 32.0 ($J_{(Rh-P)} = 171.1$ Hz).

### 7.12. Synthesis of **15c**

To a solution of 3.22 g (10.0 mmol) of **3** in 40 ml of $CH_2Cl_2$ 1.22 g (10.0 mmol) of benzeneboronic acid, dissolved in 60 ml of $CH_2Cl_2$, was added. The solution was heated to reflux for 0.5 h. After removal of the solvent in vacuo (30 °C, 1 mbar) **15c** was obtained as a colorless solid. Yield: 4.0 g (99%).

**15c**, Anal. Found: C, 73.04; 4.63. $C_{25}H_{18}BO_3P$ (408.2). Calc.: C, 73.56; H, 4.44%. MS: *m*/*e* 408, 407 ($^{11}B$, $^{10}B$) [$M^+$]. $^1H$-NMR ($CD_2Cl_2$, $\delta$): 6.0–7.2 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 118.2 (10.1), 128.1 (26.3), 104.6 (9.1), 154.3, 109.2 (7.1), 132.2 (18.2), 128.9 (10.1), 124.7 (22.2), 119.9 (7.1), 120.1, 124.9 (Ph), 118.9 (Ph), 121.2 (Ph), 163.4 (CO); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): −6.4.

### 7.13. Synthesis of **16** and **17**

5.51 g (50.0 mmol) of phenylphosphine, 13.1 g (50.0 mmol) of 3-iodo-4-methylbenzoic acid and 10.12 g (100.0 mmol) of $NEt_3$ were dissolved in 170 ml of acetonitrile. After addition of a solution of 51.8 mg (50 μmol) of tris(dibenzylideneacetone) dipalladium chloroform adduct and 41.3 mg (100 μmol) of 1,3-bis(phenylphosphino)propane in 15 ml of acetonitrile the solution was heated to 90 °C for 48 h. Thereafter, all volatiles were removed in vacuo (30 °C, 1 mbar). The residue was dissolved in 200 ml of 0.5 N NaOH. After extraction with diethylether (160 ml) and *n*-hexane (50 ml), the solution was acidified with HCl until a pH value of ca. 2 was reached. The precipitate formed was separated by filtration, washed with 150 ml of water and dried in vacuo. For further purification, colorless **16** was recrystallized from $CH_2Cl_2$. Yield: 9.4 g (77%).

**16**, Anal. Found: C, 68.45; H, 5.48. $C_{14}H_{13}O_2P$ (244.2). Calc.: C, 68.85; H, 5.36%. MS: *m*/*e* 244 [$M^+$]. $^1H$-NMR ($CDCl_3$, $\delta$): 2.5 ($CH_3$), 5.3 (223, PH), 7.1–8.0 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 136.4 (8.1), 147.9 (17.1), 130.3 (3.0), 130.6, 127.2 (3.0), 132.5 (10.1), 135.1 (12.1), 134.3 (17.2), 128.6 (7.1), 128.9, 172.0 (CO), 21.8 (14.2, $CH_3$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): −46.5 (223.0).

The tertiary phosphine **17** was obtained in a procedure analogous to that above using 2.44 g (10.0 mmol) of **16**, 2.48 g (10.0 mmol) of 3-iodobenzoic acid, 4.05 g (40 mmol) of $NEt_3$ and 30 ml of acetonitrile. The catalyst used was of palladium(II)acetate (2.2 mg, 10 μmol). **17** was obtained using the same work up procedure as above as an off-white powder. Yield: 2.93 g (81%).

**17**, Anal. Found: C, 68.97; H, 4.91. $C_{21}H_{17}O_4P$ (364.3). Calc.: C, 69.23; H, 4.70%. MS: *m*/*e* 264 [$M^+$]. $^1H$-NMR ($d_6$-DMSO, $\delta$): 1.5 ($CH_3$), 6.3–7.3 (arom. H); $^{13}C\{^1H\}$-NMR ($d_6$-DMSO, $\delta$): (C1–C10) 135.8 (13.1), 147.1 (25.3), 128.3, 133.5, 128.1, 128.8, 134.4 (9.1), 133.5 (20.2), 129.8 (8.1), 129.8; $C_6H_4$–3-COOH: 136.1 (11.2), 134.7 (24.3), 130.8 (8.1), 128.3, 128.2, 137.4 (16.2), 166.3 (COOH), 166.2 (COOH), 20.6 (20.2, $CH_3$); $^{31}P\{^1H\}$-NMR ($d_6$-DMSO; $\delta$): −12.9.

### 7.14. Synthesis of **18**

2.27 g (8.72 mmol) of bis-1,3-phenylphosphinopropane and 1.96 g (20.0 mmol) of KOAc were dissolved in 50 ml of *N*,*N*-dimethylacetamide. After addition of 0.9 ml of $Pd(OAc)_2$ solution in *N*,*N*-dimethylacetamide (10 μmol $ml^{-1}$) the mixture was heated to 130 °C for 48 h. The reaction mixture was poured into 300 ml of water and the precipitate formed was extracted with three aliquots of 20 ml of $CH_2Cl_2$.

The organic phase was washed with 30 ml of water and dried over $Na_2SO_4$. The residue obtained after removal of the solvent was suspended in 10 ml of methanol, and dilute HCl (10%) was added until a pH value of ca. 4 was reached. After filtration the solid material was recrystallized from methanol. Thereby an enrichment of one diastereoisomer (I) in a 8:3 ratio was achieved ($\delta = -34.15$ (I), $-34.28$ (II)). Yield: 2.5 g (65%).

**18**, Anal. Found: C, 73.40; H, 6.51; N, 6.49. $C_{27}H_{28}N_2P_2$ (442.5). Calc.: C, 73.29; H, 6.39; N, 6.33%. $^1$H-NMR ($CDCl_3$, $\delta$): 1.7, 2.2 ($C_3H_6$), 3.6 ($NH_2$), 6.6–7.4 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 119.42 (9.9), 119.44 (10.1), 150.2 (18.9), 115.3 (2.7), 130.2, 118.6 (2.5), 132.6 (3.7), 137.9 (10.2), 131.9 (17.6), 128.4 (6.5), 128.2, 28.0 (23.6, $CH_2$), 22.39 (17.3, $CH_2$), 22.35 (17.4, $CH_2$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-34.3$, $-34.2$.

### 7.15. Synthesis of *19a* and *19b*

To a solution of 24.73 g (87.4 mmol) or 25.0 g (88.0 mmol) of 2-bromoiodobenzene and 16.27 g (87.4 mmol) of $Ph_2PH$ or 4.85 g (44.0 mmol) of $PhPH_2$ in 200 ml of toluene 9.8 g (97.0 mmol) or 17.8 g (194.0 mmol) of triethylamine was added. After addition of 0.50 g (0.4 mmol) or 1.05 g (0.9 mmol) of $Pd(PPh_3)_4$, respectively, the mixtures were stirred at 80 °C for 12 h. The solvent was removed in vacuo (50 °C, 0.1 mbar) and the remaining residue was dissolved in 150 ml of $CH_2Cl_2$. The solution was washed with two aliquots of 150 ml of water and dried over $MgSO_4$. The residues left after evaporation of $CH_2Cl_2$ were purified by short path distillation at 200–300 °C. **19a** was obtained as a colorless solid. For a further purification **19b** was recrystallized from ethanol/water. Yield: 28.0 g (94%) **19a**, 15.7 g (85%) **19b**.

**19a**, $C_{18}H_{14}BrP$ (341.2). $^1$H-NMR ($CDCl_3$, $\delta$): 6.8–7.6 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 138.9 (12.2), 129.9 (30.5), 132.9 (2.0), 130.0, 127.3, 134.3, 135.8 (11.2), 133.9 (19.3), 128.5 (7.1), 128.9; $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-3.5$.

**19b**, Anal. Found: C, 51.61; H, 3.19. $C_{18}H_{13}Br_2P$ (420.1). Calc.: C, 51.46; H, 3.12%. MS: $m/e$ 422 ($^{81}$Br, $^{81}$Br), 420 ($^{79}$Br, $^{81}$Br), 418 ($^{79}$Br, $^{79}$Br) [$M^+$]. $^1$H-NMR ($CDCl_3$, $\delta$): 6.8–7.7 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 137.8 (11.2), 129.9 (33.6), 132.9 (2.0), 130.3, 127.4, 134.4, 134.5, 134.2 (21.4), 128.7 (7.1), 129.3; $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-2.7$.

### 7.16. Synthesis of *20a* and *20b*

A suspension of 2.73 g (8.0 mmol) of **19a** and 2.21 g (16.0 mmol) of potassium carbonate in 100 ml of toluene was charged with 1.20 g (8.8 mmol) of 2- or 4-toluneboronic acid, respectively. After addition of 0.01 g (0.6 mol%) of palladium(II) acetate the mixtures were stirred at 80 °C for 3 days. Thereafter, all volatiles were removed in vacuo. Water (100 ml) and $CH_2Cl_2$ (100 ml) were added to the remaining residue. The organic phase was separated and washed with 50 ml of water and three aliquots of a 1 M aqueous solution of KCN. After drying the organic phase with $MgSO_4$, the solvent was evaporated. **20a** and **20b** were obtained as oily residues. **20b** could be recrysallized from ethanol–water. Yield: 1.78 g (63%) **20b**.

**20a**, Anal. Found: C, 84.85; H 6.11. $C_{25}H_{21}P$ (352.4). Calc.: C, 85.21; H, 6.00%. MS: $m/e$ 352 [$M^+$]. $^1$H-NMR ($CDCl_3$, $\delta$): 2.2 ($CH_3$), 6.9–7.5 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 137.2 (11.2), 147.6 (30.5), 130.3 (3.1), 128.7, 129.7 (5.1), 133.8 (20.3), 136.7 (11.2), 136.9 (10.2), 133.9 (19.3), 133.8 (20.3), 128.4 (5.1), 128.3, 128.2, 141.0 (*o*-tolyl), 135.7 (*o*-tolyl), 129.6 (*o*-tolyl), 127.5 (*o*-tolyl), 124.8 (*o*-tolyl), 127.3 (*o*-tolyl), 20.4 (4.1, $CH_3$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-11.7$.

**20b**, Anal. Found: C, 84.02; H 5.89. $C_{25}H_{21}P$ (352.4). Calc.: C, 85.21; H, 6.00%. MS: $m/e$ 352 [$M^+$].$^1$H-NMR ($CDCl_3$, $\delta$): 2.5 ($CH_3$), 6.9–7.5 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 135.7 (14.3), 148.3 (29.5), 129.5, 130.1, 129.5, 134.2, 137.8 (11.2), 133.8 (20.3), 128.3 (6.1), 128.6, 138.8 (6.1, *p*-tolyl), 127.1 (*p*-tolyl), 130.1 (*p*-tolyl), 136.7 (*p*-tolyl), 21.1 ($CH_3$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-12.3$. **20b** could not be obtained in a satisfying analytical purity.

### 7.17. Synthesis of *21a* and *21b*

These compounds have been obtained in an analogous way as **20a** and **20b**. Thus 4.20 g (10.0 mmol) of **19b**, 5.67 g (41.0 mmol) of potassium carbonate, 0.02 g (1.2 mol%) of palladium(II) acetate and 3.13 g (23.0 mmol) of 2- or 4-toluneboronic acid, respectively, in 100 ml of toluene gave **21a** and **21b** after recrystallization from ethanol–water. Yield: 0.95 g (22%) **21a** or 2.28 g (52%) **21b**.

**21a**, Anal. Found: C, 86.78; H, 6.24. $C_{32}H_{27}P$ (442.5). Calc.: C, 86.85; H, 6.15%. MS: $m/e$ 442 [$M^+$]. $^1$H-NMR ($CDCl_3$, $\delta$): 1.6 ($CH_3$), 1.8 ($CH_3$), 2.0 ($CH_3$), 2.2 ($CH_3$), 6.4–7.5; $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): 20.5 (5.1, $CH_3$), 20.1 (4.1, $CH_3$), 19.8 (3.0, $CH_3$), 19.6 (5.1, $CH_3$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-17.1$, $-20.1$, $-20.2$.

**21b**, Anal. Found: C, 86.50; H, 6.12. $C_{32}H_{27}P$ (442.5). Calc.: C, 86.85; H, 6.15%. MS: $m/e$ 442 [$M^+$]. $^1$H-NMR ($CDCl_3$, $\delta$): 2.4 ($CH_3$), 6.9–7.5 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, $\delta$): (C1–C10) 136.4 (14.3), 148.0 (29.5), 129.9 (4.1), 128.1, 129.4 (3.1), 134.3, 137.6 (13.2), 134.0 (19.3), 128.2 (6.1), 128.2, 138.7 (6.1, *p*-tolyl), 127.0 (*p*-tolyl), 128.4 (*p*-tolyl), 136.3 (*p*-tolyl), 21.1 ($CH_3$); $^{31}P\{^1H\}$-NMR ($CDCl_3$, $\delta$): $-18.8$.

### 7.18. X-ray structural analyses of **3** and **6**

#### 7.18.1. Crystal structure analysis of $Ph_2P–C_6H_3–3\text{-}COOH–4\text{-}OH$ (**3**)

A crystal of **3** was mounted in a glass capillary. X-ray data were collected using a Siemens P4/V diffractometer equipped with a graphite monochromator and employing Mo–$K_\alpha$ radiation. The structure was solved using direct methods and was refined by full matrix least squares. Crystal data and refinement details are given in Table 2. The program SHELXTL was used for the refinement.

### 7.19. Crystal structure analysis of $Ph_2P–C_6H_4–2\text{-}i\text{-}Pr$ (**6**)

A crystal of **6** was glued to a glass fiber. X-ray data were measured with a Siemens P3 diffractometer equipped with a graphite monochromator and employing Mo–$K_\alpha$ radiation. The structure was solved by direct methods and was refined with a SHELXTL program package (version 5.03) with non-hydrogens anisotropic and hydrogens isotropic. Crystal data and refinement details are given in Table 2.

Table 2
Crystal and refinement data for **3** and **6**

| | **3** | **6** |
|---|---|---|
| Chemical formula | $C_{19}H_{15}O_3P$ | $C_{21}H_{21}P$ |
| Formula weight | 322.3 | 304.4 |
| Temperature (K) | 293(2) | 293(2) |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $P\bar{1}$ | *Pbca* |
| $a$ (Å) | 5.716(1) | 6.538(7) |
| $b$ (Å) | 11.054(2) | 12.519(5) |
| $c$ (Å) | 13.397(3) | 16.860(7) |
| $\alpha$ (°) | 95.91(3) | 90 |
| $\beta$ (°) | 96.31(3) | 90 |
| $\gamma$ (°) | 92.91(3) | 90 |
| $V$ (Å$^3$) | 835.2(3) | 3490.6(8) |
| $Z$ | 2 | 8 |
| $D_{calc}$ (mg m$^{-3}$) | 1.282 | 1.158 |
| Absorption coefficient (mm$^{-1}$) | 0.176 | 0.152 |
| $F(000)$ | 336 | 1296 |
| Crystal size (mm) | $0.58 \times 0.46 \times 0.32$ | $0.20 \times 0.24 \times 0.32$ |
| $\theta$-range (°) | 2.28–24.99 | 2.37–20.04 |
| Index ranges | $0 \le h \le 6$, $-13 \le k \le 13$, $-15 \le l \le 15$ | $0 \le h \le 15$, $0 \le k \le 12$, $-16 \le l \le 0$ |
| Reflections collected | 3252 | 1894 |
| Independent reflections | 2931 [$R_{int} = 0.0284$] | 1634 |
| Observed reflections [$I > 2\sigma(I)$] | 2207 | 826 |
| Absorption correction | Semiempirical | None |
| Max/min transmission | 0.733–0.592 | – |
| Parameters | 216 | 204 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0408$, $wR_2 = 0.0944$ | $R_1 = 0.0322$, $wR_2 = 0.0400$ |
| $R$ indices (all data) | $R_1 = 0.0608$, $wR_2 = 0.1064$ | $R_1 = 0.0916$, $wR_2 = 0.0465$ |
| Largest difference peak and hole (e Å$^{-3}$) | 0.200/−0.188 | 0.14/−0.14 |

## 8. Supplementary material

Further details of the crystal structure investigations on **3** and **6** are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2, IET, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the depository number CCDC 147286 and CCDC 147048 for **3** and **6**, respectively.

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