Journal of Organometallic Chemistry 695 (2010) 2618–2628

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Novel phosphite palladium complexes and their application in C–P cross-coupling reactions

Jie Li [a], Martin Lutz [b], Anthony L. Spek [b], Gerard P.M. van Klink [a,1], Gerard van Koten [a], Robertus J.M. Klein Gebbink [a,*]

[a] Chemical Biology and Organic Chemistry, Debye Institute for Nanomaterials Science, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
[b] Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

ARTICLE INFO

Article history:
Received 22 April 2010
Received in revised form
12 August 2010
Accepted 20 August 2010
Available online 6 September 2010

Keywords:
Palladation
Orthometallation
Palladacycle
Pincer complex
C–P cross-coupling

ABSTRACT

A mono- and a 1,3-bis-phosphite arene ligand based on 2,2′-biphenol have been synthesized in order to study the synthesis of the corresponding palladium(II) complexes starting from different Pd precursors. Novel bis-phosphite palladium complex **1** [$PdCl_2(L)_2$] (L = dibenzo[d,f][1,3,2]dioxaphosphepin, 6-phenoxy), *C,P*-chelate bonded monophosphite palladium complex **2** [$Pd(\kappa_2\text{-}L)(\mu\text{-}Cl)]_2$, and PCP-pincer palladium complex **3** have been prepared from these ligands in promising to excellent yields (50–95%). Additionally, complexes **1** and **3** have been characterized by X-ray crystal structure determinations. The application of 2,6-bis-phosphite pincer palladium(II) complex **3** in C–P cross-coupling between diphenylphosphine-borane and a wide range of various aryl iodides under very mild conditions is reported. Kinetic investigations indicate that **3** merely acts as a pre-catalyst and that Pd nanoparticles are the actual catalytically active species.

1. Introduction

In the past decades, phosphine ligands [1], as a major type of phosphorus donor ligands, have received much attention due to their excellent performance in transition metal catalyzed organic transformations [2]. The development of non-oxygen sensitive, electron-deficient phosphite ligands, and their corresponding metallated complexes, have become of increasing interest as supplements to phosphine ligands [3]. Phosphite ligands can be prepared from commercially available PCl_3 and a variety of different alcohols, which allows easy access to a great variety of ligands with various steric and electronic properties. For instance, Bedford et al. recently reported the synthesis of a series of triarylphosphite ligands $P(OAr)_3$ and their facile ortho-metallation with late transition metals, along with their remarkably catalytic activity in C–C bond formations [4]. Additionally, phosphite pincer complexes have been recently reported [4]. The excellent catalytic activities in Suzuki, Heck and allylation reactions [5] stimulated the further development of these phosphite-derived pincer complexes.

Transition metal catalyzed cross-coupling reactions are particularly important and powerful tools to realize chemical bond formations. In the past decades, numerous examples of C–C, C–N, C–S and C–P cross-coupling reactions have been developed by taking advantage of rationally designed ligands, appropriate transition metals and optimized reaction conditions [6]. Among the large number of documented ligands bearing a variety of diversified donors, phosphorus donor comprising ligands, especially, tertiary phosphine ligands, have held a core position in the domain of ligands design and catalysis [7]. Therefore, the development of new methodologies to easily access tertiary phosphines or their derivatives via direct P–C bond forming reactions became more and more desirable [8]. For instance, a versatile $Pd(OAc)_2$/1,1′-bis(diisopropylphosphino)ferrocene-catalyzed cross-coupling of secondary phosphines with aryl halides was developed by Buchwald and Murata [9]. Zhao and coworkers reported an efficient copper-catalyzed approach for the P-arylation of primary and secondary organophosphorus compounds using commercially available and inexpensive proline and pipecolinic acid as ligands. This method provides an entry to arylphosphonates, arylphosphinates and arylphosphine oxides [10]. To the best of our knowledge, pincer complexes have not been studied in C–P cross-coupling

* Corresponding author. Tel.: +31 30 253 1889; fax: +31 30 252 3615.
E-mail address: r.j.m.kleingebbink@uu.nl (R.J.M. Klein Gebbink).
[1] Present address: DelftChemTech, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.08.026

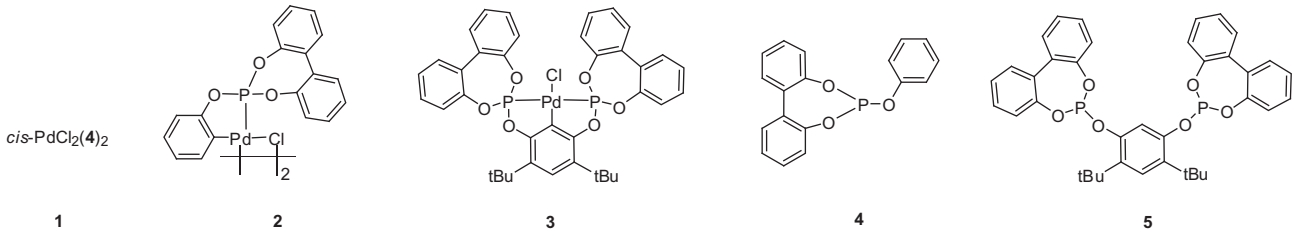


Fig. 1. Entitled phosphite Pd complexes **1**–**3** and phosphite ligands **4** and **5**.

reactions for the preparation of tertiary phosphine-boranes, though, their remarkable catalytic performances in Heck [11], Suzuki [12] and Sonogashira [13] reactions have been carefully studied and are well documented.

In this study, 2,2′-biphenol was selected as an inexpensive and commercially available building block for the preparation of monodentate phosphite ligand **4** and bis-phosphite pincer ligand **5** (Fig. 1).

The corresponding metal complexes **1**–**3** were obtained in promising to good yields by reacting ligands **4** and **5** with different metal precursors under various reaction conditions. Full details on the synthesis and structural characterization of these ligands and complexes are described. Furthermore, we report the first examples of the application of phosphite PCP-pincer complex in C–P cross-coupling reactions.

2. Results and discussion

2.1. Synthesis and characterization of phosphite palladium complexes *1* and *2*

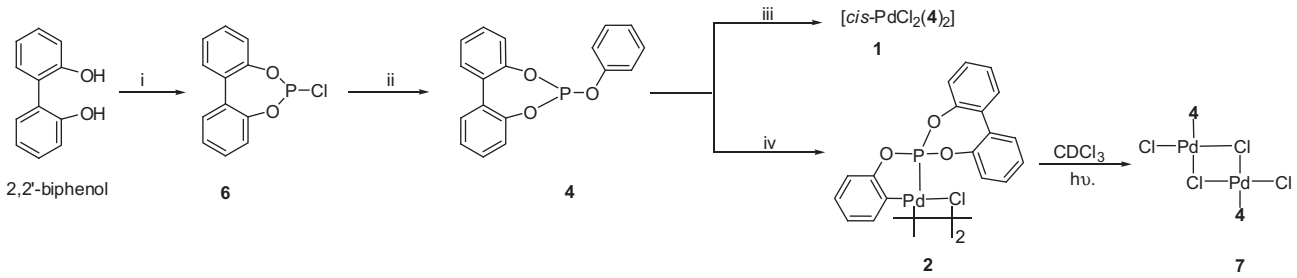
In order to synthesize monodentate ligand **4**, 2,2′-biphenol was refluxed in freshly distilled PCl_3 for 2 h to yield phosphorochloridite **6** in quantitative yield (Scheme 1). Without purification, **6** was subsequently reacted with phenol in the presence of triethylamine at reflux in toluene to afford the desired monodentate phosphite ligand **4** in good yield. Ligand **4** was reacted with different Pd(II) precursors under various conditions to give the corresponding phosphite Pd complexes **1** and **2**. For example, *cis*-$PdCl_2$(**4**)$_2$ (**1**) was obtained in excellent yield (95%) by reacting 2 equivalents of phosphite ligand **4** with 1.0 equivalent of $PdCl_2(MeCN)_2$ in dichloromethane at room temperature. Suitable, colorless crystals of **1** were obtained by slow vapor diffusion of methanol into a dichloromethane solution of **1** at room temperature. The structure of **1** was determined by single crystal X-ray structure determination. As shown in Fig. 2, complex **1** adopts a typical *cis*-configuration, in which two chloride ligands and two phosphite ligands both occupy mutual *cis*-positions (Cl–Pd–Cl angles of 92.54 (3) and 91.92(3)°, and P–Pd–P angles of 95.36(3) and 95.74(3)°, respectively). As expected, when steric effects of the phosphite ligands do not override electronic effects, the weakly π-basic chloride ligands are preferentially positioned in *trans*-positions with respect to the phosphite ligands by taking advantage of their strongly π-acidic feature [4d,e,14].

In addition to *cis*-bis-phosphite Pd(II) complex **1**, ortho-palladated complex **2** was prepared in good yield by refluxing ligand **4** in toluene overnight in the presence of a stoichiometric amount of $PdCl_2$ in accordance with the procedure published by Bedford et al. [4a,b]. It is worth pointing out that other small size phosphite ligands, such as triphenylphosphite, do not yield ortho-metallated complexes under the same reaction conditions [4d,14]. ^{13}C NMR analysis showed a signal at δ 150.1 ppm, which is very typical for the C_{ipso} of C–Pd σ-bonds in ortho-metallated complexes [4,5,14]. MALDI-TOF MS data confirmed the formation of a dimeric complex. ^{31}P NMR spectra in $CDCl_3$ at 25 °C showed complex **2** to be a mixture of *cis*- and *trans*-isomers, as was also reported for other ortho-palladated complexes [4,5,14]. Both ^{31}P and ^{1}H NMR spectra showed rather broad peaks at 25 °C, which could be due to the facile interchange of *cis*- and *trans*-isomers and the conformational flexibility of the seven-member ring in the phosphite ligand at room temperature [4d]. The ratio of the two isomers in solution at room temperature was estimated as 1:15 (*cis*:*trans*) by comparing the ^{31}P NMR signals, which is rather high with respect to reported analogues [4e,14]. This is presumably due to the small and rigid 2,2′-biphenol moiety that does not impose significant steric congestions in the *trans*-isomer.

Interestingly, upon standing for 10 days a solution of complex **2** in $CDCl_3$ gradually showed the formation of dimer **7** that contains the non-orthometallated ligand. As shown in Fig. 3, the C–Pd bonds in **2** have been split. It is well documented that palladacycles are sensitive to protonolysis by HCl in $CDCl_3$ solution in the presence of light in air [4d].

2.2. Synthesis and characterization of phosphite PCP-pincer palladium complex *3*

In contrast to the relatively straightforward synthesis of phosphine and phosphinite PCP-pincer ligands [15], the metallation *via* direct C–H activation of phosphite pincer ligands in order to



Scheme 1. Synthesis of phosphite Pd complexes **1** and **2**. Reaction conditions and reagents: i) PCl_3, reflux, 2 h, quantitative yield; ii) phenol, Et_3N, toluene, reflux, 2 h, 88%; iii) $PdCl_2(MeCN)_2$, DCM, r.t., 1 h, 95%; iv) $PdCl_2$, toluene, reflux, 16 h, 50%.

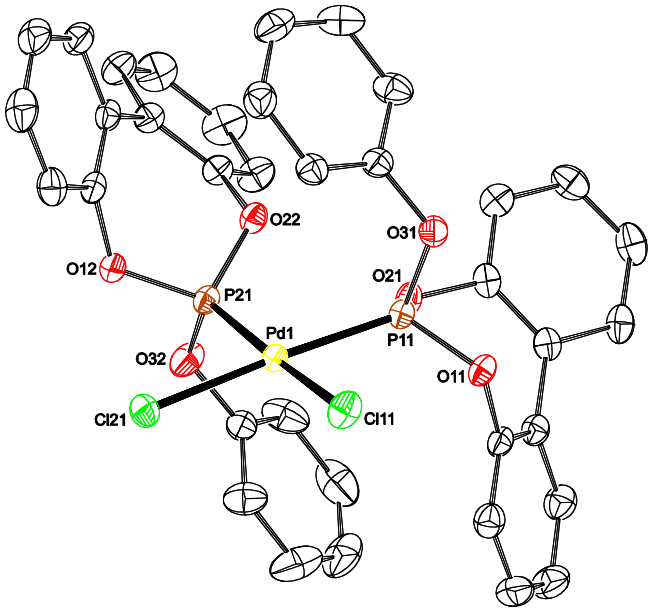


Fig. 2. Displacement ellipsoid plot of **1** in the crystal (50% probability level). Hydrogen atoms have been omitted for clarity. Only one of two independent molecules is shown. Characteristic bond distances (Å) and bond angles (°) in **1** [second molecule in square brackets]: Pd1–Cl11 = 2.3388(7) [2.3246(7)], Pd1–Cl12 = 2.3298(7) [2.3303(7)], Pd1–P11 = 2.2105(7) [2.2154(7)], Pd1-P21 = 2.2207(7) [2.2115(7)], Cl11–Pd1–Cl21 = 92.54(3) [91.92(3)], P11-Pd1-P21 = 95.36(3) [95.74(3)].

prepare phosphite PCP-pincer complexes is rather difficult [5b]. A small number of phosphite pincer palladium complexes have been prepared by the oxidative insertion of a zerovalent Pd precursor (*e.g* $Pd_2(dba)_3.CHCl_3$) into C–I or C–Br bonds [5a,d]. Recently, Bedford and coworkers found that the ortho-metallation *via* C–H activation of phosphite PCP-pincer ligands could be dramatically enhanced by using encumbered 4,6-di-*tert*-butylbenzene-1,3-diol as the key building block [5b,16]. As elaborated in Scheme 2, a novel pincer ligand **5** was prepared by following the same synthetic protocol as mentioned above. Reacting phosphorochloridite **2** with 4,6-di-*tert*-butylbenzene-1,3-diol in the presence of Et_3N at 110 °C in toluene afforded pincer ligand **5** in high yield (88%). Reaction of ligand **5** with $PdCl_2(MeCN)_2$ in the presence of Et_3N in dichloroethane for 2 h at refluxing temperature smoothly yielded the desired pincer complex **3** in good yield (65%). It seems that the more hindered di-*tert*-butylresorcinol-based ligand **5** prevents the formation of polymers and/or decreases the degree of polymerization upon heating as documented for the BINOL-derived pincer ligand analogue [5b].

Colorless crystals of **3** were obtained by slow diffusion of hexanes into a THF solution of **3** at room temperature. The structure of **3** in the solid state was determined by single crystal X-ray structure determination. As shown in Fig. 4, the complex adopts a very typical *mer*-pincer configuration geometry. The palladium atom is located at the central position of a slightly distorted square-planar structure, with the chloride group occupying a *trans*-position to the *ipso*-carbon atom. The two phosphorus donors are mutually located in *trans*-positions, with P–Pd–P angles of 159.600 (17) and 159.313(17)°, respectively. The two independent molecules in the crystal have opposite configurations on phosphorus, pointing to the fluxional behavior of these stereocenters, as is also indicated by solution NMR-data. A similar fluxional behavior is also present in the other Pd complexes.

2.3. Bis-phosphite pincer palladium complex catalyzed C–P cross-coupling reactions

Recently, secondary phosphine-borane adducts have been widely used as versatile substrates to perform C–P cross-coupling reactions due to their facile preparation, inertness towards oxygen and moisture, and good reactivities [17,18]. Thus, diphenylphosphine-borane was employed as model phosphine substrate and reaction optimization was carried out using a slight excess of Ph-I (1.05 equivalent) in the presence of 2 equivalents of K_2CO_3 as base and Pd-phosphite complexes **1**–**3** (5 mol%) as catalysts under various reaction conditions (Table 1).

According to the experimental data showed in Table 2, the chemical yields of the product $PPh_3{\cdot}BH_3$ were highly solvent-dependent when using **3** as the catalyst. The reaction in MeCN at 40 °C proceeded with 50% chemical yield, whereas the reaction in toluene did not furnish any conversion and the reaction merely gave a poor yield of 10% in THF (Table 1, entry 3 *vs* entries 1 and 2). Possibly, the reaction requires a polar and coordinating solvent to

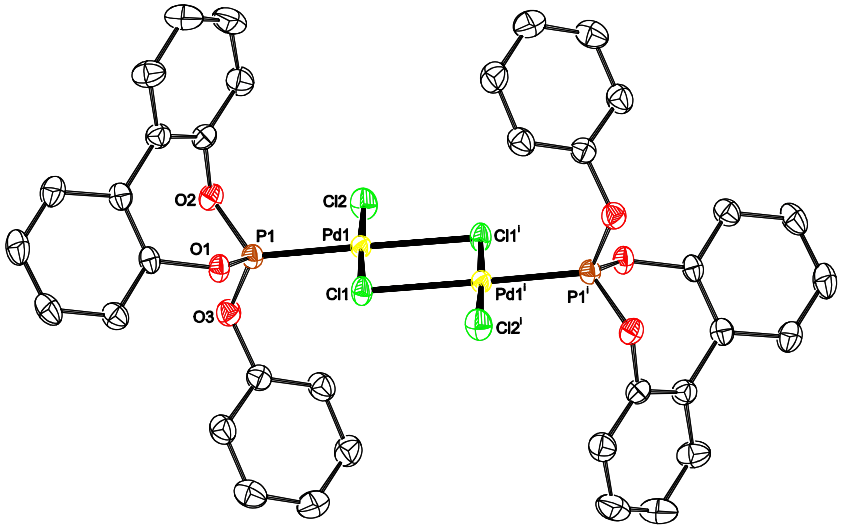
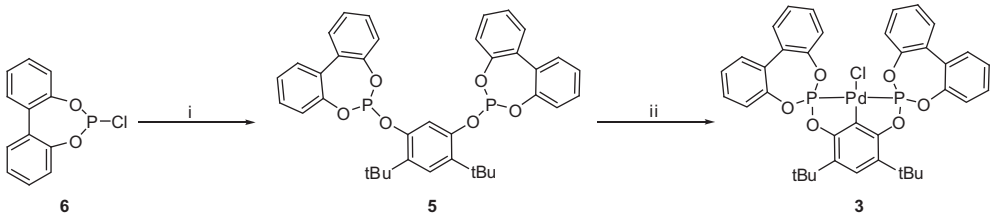


Fig. 3. Displacement ellipsoid plot of **7** in the solid state (50% probability level). Hydrogen atoms and co-crystallized $CDCl_3$ have been omitted for clarity. Symmetry operation i: $1-x$, $1-y$, $1-z$. Characteristic bond distances (Å) and bond angles (°) in **7**: Pd1–Cl1 = 2.3133(4), Pd1–Cl2 = 2.2749(4), Pd1–$Cl1^i$ = 2.3944(4), Pd1–P1 = 2.1783(4), P1–Pd1–Cl1 = 94.437(14), P1–Pd1–Cl2 = 87.353(15), Cl2–Pd1–$Cl1^i$ = 91.938(14).



Scheme 2. Synthesis of phosphite PCP-pincer complex **3**. Reaction conditions and reagents: i) 4,6-di-*tert*-butylbenzene-1,3-diol, Et_3N, toluene, reflux, 2 h, 88%; ii) $PdCl_2(MeCN)_2$, Et_3N, $ClCH_2CH_2Cl$, 80 °C, 2 h, 65%.

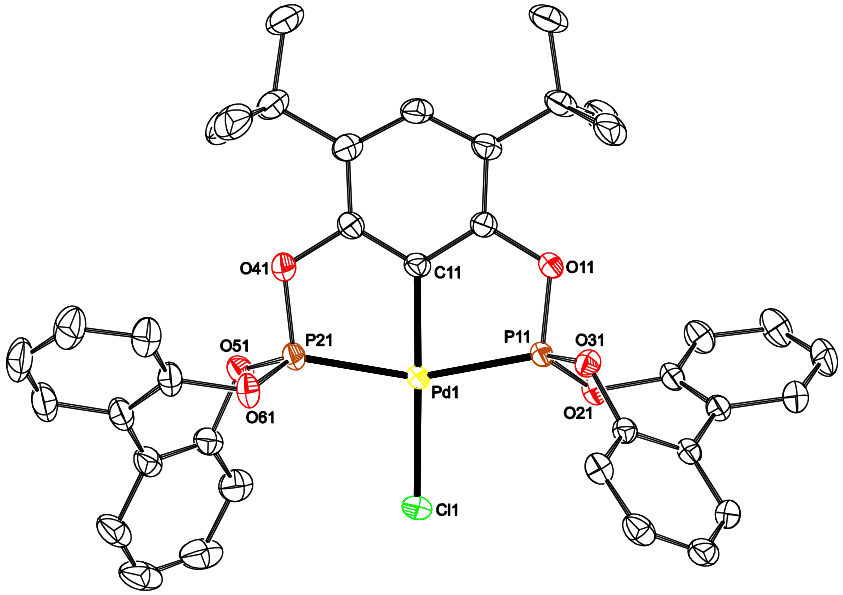
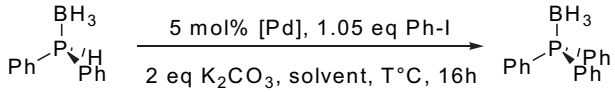


Fig. 4. Displacement ellipsoid plot of **3** in the solid state (50% probability level). Hydrogen atoms and THF solvent molecules have been omitted for clarity. Only one of two independent molecules is shown. Characteristic bond distances (Å) and bond angles (°) in **3** [second molecule in square brackets]: Pd1–C11 = 2.0089(17) [2.0080(16)], Pd1–Cl1 = 2.3429(5) [2.3460(5)], Pd1-P11 = 2.2539(4) [2.2437(4)], Pd1–P21 = 2.2517(5) [2.2743(5)], C11–Pd1–Cl1 = 176.11(5) [176.90(5)], P11–Pd1–P21 = 159.600(17) [159.313 (17)].

Table 1
Pd-catalyzed C–P coupling between $Ph_2PH{\cdot}BH_3$ and phenyl iodide; reaction optimization.[a]



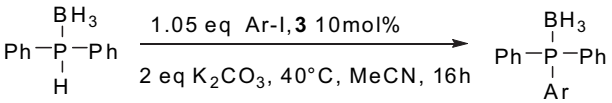
Entry	Cat.	Condition (T °C/Solvent)	Yield[b] (%)
1	**3**	40/Toluene	0
2	**3**	40/THF	10
3	**3**	40/MeCN	50
4[c]	**3**	40/MeCN	0
5	**2**	40/MeCN	40
6	**1**	40/MeCN	90
7	**3**	82/MeCN	44
8[d]	**3**	50/MeCN	70
9[e]	**3**	40/MeCN	>95

[a] Reaction conditions as follows unless otherwise stated: 0.105 mmol of Ph-I, 0.1 mmol of $Ph_2PH(BH_3)$, 5 mol% catalyst, 0.2 mmol of K_2CO_3, 1 mL of solvent, 16 h, under N_2.
[b] ^{31}P NMR yield with diethyl ethylphosphonate as internal standard.
[c] In air.
[d] 7.5 mol% [Pd] catalyst loading.
[e] 10 mol% [Pd] catalyst loading.

dissolve the inorganic base K_2CO_3 and to stabilize the catalytically active palladium species. Interestingly, although both the diphenylphosphine-borane substrate and the triphenylphosphine-borane product are resistant towards oxidation and hydrolysis in air, the exclusion of air is crucial to afford conversion (Table 1, entry 4). Pd dimer complex **2** gave slightly lower yield in contrast to pincer complex **3** (Table 1, entry 3 *vs.* entry 5), while bis-phosphite palladium complex **1** gave 90% yield (Table 1, entry 6). In this paper, we focused on the investigation of the catalytic activity of pincer complex **3**. Elevated temperatures did not improve the yield when using **3**. In contrast, it led to an increased formation of many by-products (Table 1, entry 7). A remarkable improvement was achieved upon progressively increasing the loading of **3** (Table 1, entries 8 and 9). Eventually, complete conversion was obtained by using 10 mol% loading of **3** in MeCN at 40 °C in the presence of 2 equivalents of K_2CO_3. It is worth pointing out that when Ph-Br and $MePhH(BH_3)$, respectively, were tested as substrates under optimized conditions, neither of them gave any conversion and starting materials were fully recovered from the reaction mixtures. To illustrate the potential of the catalytic procedure, a substrate library of 19 different aryl iodides was evaluated by using the optimized conditions (Table 2).

As shown in Table 2, PCP-pincer complex **3** smoothly catalyzes C–P cross-couplings of diphenylphosphine-boranes and a wide scope of aryl iodide substrates with promising to excellent isolated yields. The model substrate, Ph-I, gave 95% yield, whereas slightly electron-enriched and *ortho*-substituted 1-iodonaphthalene

Table 2
Phosphite PCP-pincer complex **3** catalyzed C–P cross-coupling reactions.[a]



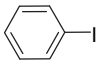
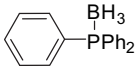
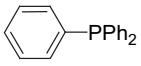
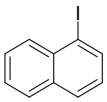
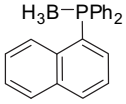
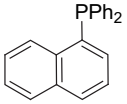
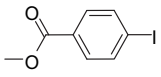
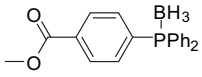
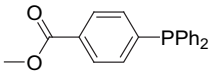
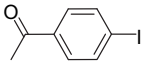
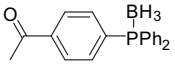
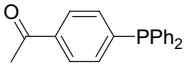
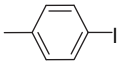
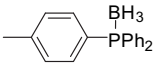
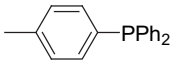
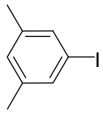
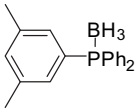
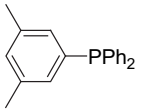
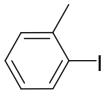
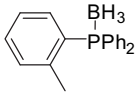
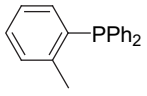
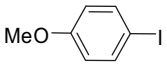
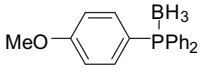
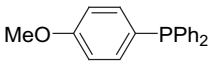
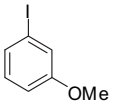
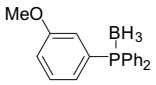
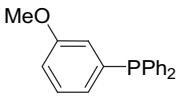
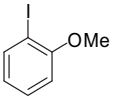
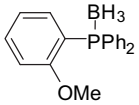
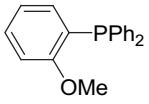
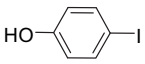
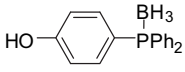
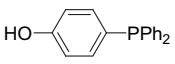
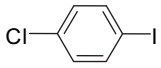
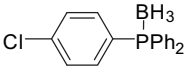
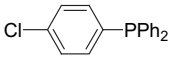
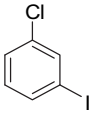
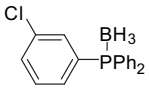
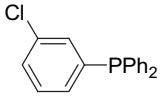
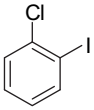
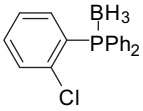
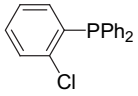
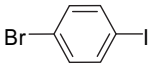
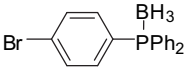
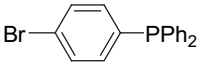
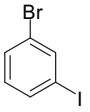
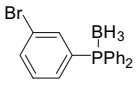
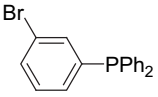
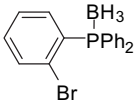
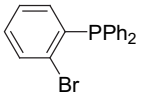
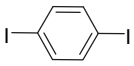
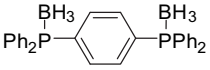
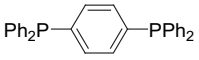
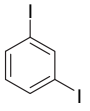
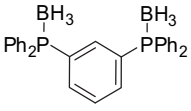
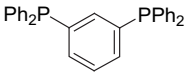
Entry	Ar-I	Phosphine-borane	Yield[b] (%)	Phosphine	Yield[c] (%)	Reference[d]
1			95		95	
2			74		95	[19]
3			98		87	[20]
4			96		91	[21]
5			95		83	[22]
6			94		72	[23]
7			50		86	[23]
8			95		79	[24]
9			87		84	[25]
10[c]			46		81	[26]
11			69		75	[27]

Table 2 (*continued*)

Entry	Ar-I	Phosphine-borane	Yield[b] (%)	Phosphine	Yield[c] (%)	Reference[d]
12			74		89	[28]
13			71		90	[29]
14			58		85	[30]
15			63		80	[31]
16			57		93	[32]
17			17		88	[33]
18[e]			95		95	[23]
19[e]			95		95	[34]

[a] Reaction conditions as follows unless otherwise stated: 0.105 mmol of Ar-I, 0.1 mmol of $Ph_2PH(BH_3)$, 0.01 mmol of **3**, 0.2 mmol of K_2CO_3, 1 mL of MeCN, 16 h, under N_2.
[b] Isolated yields of tertiary phosphine-boranes.
[c] Isolated yields of tertiary phosphines.
[d] References are provided for the original synthesis of the reaction products.
[e] 0.1 mmol of diiodobenzene, 0.21 mmol of $Ph_2PH(BH_3)$ and 0.021 mmol of **3** were used.

decreased the yield by 20% (Table 2, entries 1 and 2). As anticipated, substrates comprising electron-withdrawing methyl acetate and acetyl functional groups afforded excellent yields (Table 2, entries 3 and 4). Moreover, substrates functionalized with electron-donating methyl and methoxyl groups on either *meta*- or *para*-positions generally did not decrease the yields (Table 2, entries 5, 6, 8 and 9). Nevertheless, *ortho*-functionalized substrates gave significantly decreased yields of about 50% (Table 2, entries 7 and 10), which could be due to steric congestion effects. Noticeably, the *para*-hydroxy functionalized substrate gave much lower yield than the *para*-methoxy group functionalized substrate (Table 2, entry 8 *vs.* entry 11), presumably because the considerably acidic phenol moiety reacts with K_2CO_3 and the resulting potassium phenolate adduct is poorly soluble in MeCN.

Since we observed that bromobenzene is not active at all in this catalytic process (*vide supra*), substrates bearing either bromine or chlorine atoms were evaluated in catalysis. The resulting products bearing carbon–halogen bonds could be potentially valuable targets for further organic transformations through subsequent cross-coupling reactions. As shown in Table 3, chlorine functionalized substrates in most cases outperformed the corresponding bromine-functionalized ones under the same reactions conditions (Table 2, entries 12 and 13 *vs.* entries 15 and 16), while the yields of desired products were generally promising in both cases. Moreover, *meta*- and *para*-functionalized substrates also outperformed *ortho*-functionalized ones as mentioned before (Table 2, entries 12 and 13 *vs.* entry 14; entries 15 and 16 *vs.* entry 17). Unfortunately, the yield was dramatically decreased to only 17% for 1-bromo-2-iodo-benzene. To our delight, besides monophosphine products, this method also works for the preparation of diphosphine products. For example, reacting 2.1 equivalents of diphenylphosphine-borane adducts to 1.0 equivalent of 1,3- or 1,4-

Table 3
Selected crystallographic data for complexes **1**, **3**, and **7**.

	1	**3**	**7**
Formula	$C_{36}H_{26}Cl_2O_6P_2Pd$	$C_{38}H_{35}ClO_6P_2Pd\cdot0.5(C_4H_8O)$ + disordered solvent	$C_{36}H_{26}Cl_4O_6P_2Pd_2\cdot2(CHCl_3)$
FW	793.81	827.50[a]	1209.84
Crystal color	Colorless	Colorless	Yellow
Crystal size [mm^3]	0.54 × 0.36 × 0.36	0.30 × 0.30 × 0.30	0.51 × 0.30 × 0.08
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	12.2961(2)	14.6466(10)	9.50019(17)
b [Å]	14.6736(3)	16.1015(7)	10.13286(18)
c [Å]	19.8556(4)	20.4137(12)	12.2159(2)
α [°]	71.927(1)	99.657(2)	80.303(1)
β [°]	72.144(1)	94.758(2)	73.343(1)
γ [°]	88.825(1)	112.789(2)	85.570(1)
V [Å^3]	3230.65(10)	4317.2(4)	1109.99(3)
Z	4	4	1
D_x [g/cm^3]	1.632	1.273[a]	1.810
Refl. meas./unique	55,800/14,758	123,398/19,826	26,489/5077
μ [mm^{-1}]	0.887	0.607[a]	1.529
Abs. corr.	Multi-scan	Multi-scan	Multi-scan
Abs. corr. range	0.49–0.73	0.61–0.83	0.72–0.89
Param./restraints	847/0	922/0	262/0
$R1/wR2$ [$I > 2\sigma(I)$]	0.0333/0.0835	0.0245/0.0705	0.0187/0.0470
$R1/wR2$ [all refl.]	0.0444/0.0876	0.0326/0.0736	0.0208/0.0481
S	1.170	1.063	1.039
Res. density [e/Å^3]	−1.18/0.62	−0.41/0.54	−0.32/0.64

[a] Derived parameters do not contain the contribution of the disordered solvent.

diiodobenzene under optimized conditions afforded the desired 1,3- or 1,4-phenylene-bis(diphenylphosphine-borane) products in excellent yields (Table 2, entries 18 and 19). Although it requires a relatively high catalyst loading (*i.e.*, 10 mol%), the present catalytic protocol can smoothly bring about the cross-coupling of diphenylphosphine-borane and aryl iodides under very mild conditions in comparison with several other protocols that rely on bidentate phosphine ligands [17d,e].

According to reported procedures, the removal of the BH_3 group can be easily accomplished by using strong acid [35] or strong base [36] under mild conditions. Recently, Hiyama et al. reported a novel benign deprotection method for phosphine-boranes under neutral conditions [26]. The procedure afforded free phosphines in excellent yields by refluxing phosphine-borane adducts with activated molecular sieves (4 Å) in an ethereal solvent (THF/MeOH 7:3 (v/v)) for 96 h (Scheme 3). Accordingly, all prepared phosphine-borane compounds were efficiently deprotected by using this procedure and all spectral data of the resulting free phosphines were fully identical to those reported in the literature (Table 2).

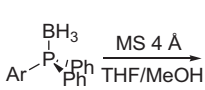
2.4. Investigations into the nature of the catalytically active species

To understand the mechanism of the reaction and to identify the catalytically active species, a reaction profile study along with poisoning tests were carried out. By means of ^{31}P NMR measurements, a reaction profile curve of the chemical yield of the product against time was obtained for the reaction of diphenylphosphine-borane and Ph-I (Fig. 5).

Fig. 5 represents a S-shaped curve, which indicates that the reaction rate varied during the catalytic process and included an introduction period as well as an accelerating period. This observation strongly suggests that complex **3** might act as a pre-catalyst, which decomposes under the reaction conditions to form a catalytically active species. While Pd-black formation was not observed during the entire procedure, the development of a deeply orange color indicated the formation of Pd^0 clusters.

To confirm this assumption, a standard poisoning test was carried out. Crabtree and Anton [37a] and Whitesides et al. [37b] independently reported that adding an excess of metallic mercury leads to the amalgamation of the surface of heterogeneous metal particles thus poisoning them, whereas in most of the cases this will not affect homogeneous catalysts. To ensure sufficient time for the mercury droplets to capture Pd nanoparticles, the experiments were carried out 10 times more diluted than the previous profile study. As depicted in Fig. 6, completely suppressed conversions were found after charging Hg at $t = 0$ or $t = 2.5$ h.

Besides the use of mercury as a poison, the protocol described by Widegren and Finke [38] predicts that when catalytic activity can be completely terminated with ≪1 equivalent of an external ligand,



Scheme 3. Deprotection of tertiary phosphine-boranes.

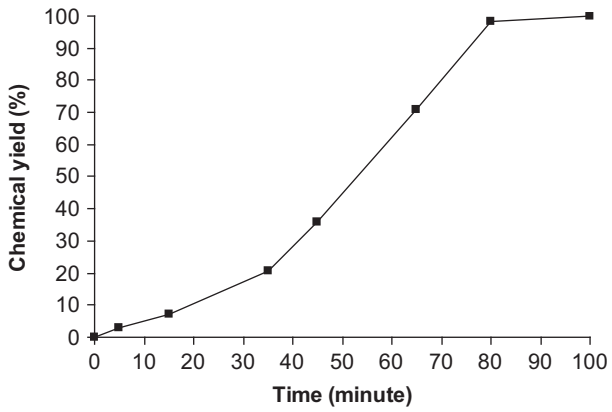


Fig. 5. Reaction profile study of the C–P cross-coupling of $Ph_2PH(BH_3)$ and Ph-I using **3** as catalyst. (Reaction conditions: 1 mmol of $Ph_2PH(BH_3)$, 1.05 mmol of Ph-I, 2 mmol of K_2CO_3, 0.1 mmol of complex **3**, 4 ml of MeCN, 40 °C, diethyl ethylphosphonate as internal standard.)

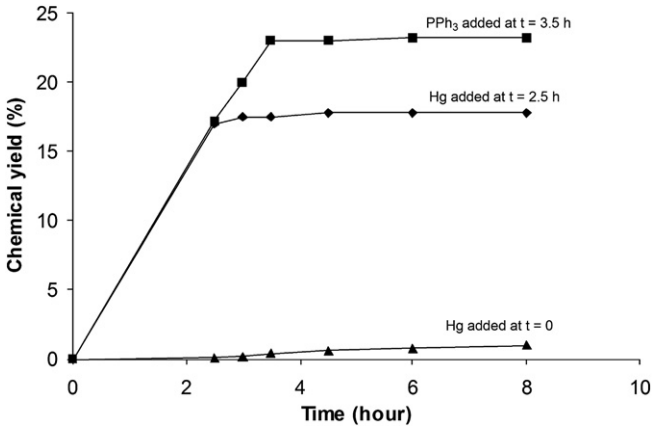
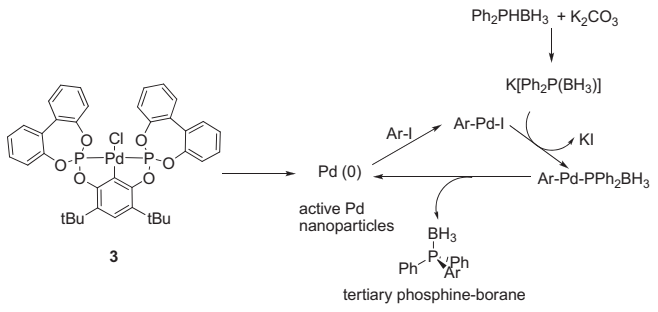


Fig. 6. Poisoning tests with Hg and PPh_3 as the inhibitors. (Reaction conditions: 0.1 mmol of $Ph_2PH(BH_3)$, 0.105 mmol of Ph-I, 0.2 mmol of K_2CO_3, 0.01 mmol of complex **3**, 4 mL of MeCN, 40 °C, diethyl ethylphosphonate as internal standard.)

such as PPh_3, that it is highly suggestive of the presence of a heterogeneous catalyst. In the case of **3**, complete conversion was obtained when 0.05 equivalent of PPh_3 was added at $t = 0$ which does not agree with the reported poisoning protocol for a heterogeneous catalyst. To understand this observation, complex **3** and 0.05 equivalent of PPh_3 were mixed in an NMR tube and the ^{31}P NMR spectrum of the resulting mixture was recorded at 40 °C. A new single peak at 24.3 ppm was observed, which corresponds to the formation of *trans*-dichlorobis(triphenylphosphine)palladium, which might be an active catalyst too for the cross-coupling of aryl iodides and secondary phosphine-boranes. Nevertheless, completely suppressed catalytic activity was observed right after adding PPh_3 at $t = 3.5$ h (Fig. 6), which is in accordance with a catalytic species of heterogeneous nature. Noticeably, PCP- [15a] and SCS- [11b,12b,39] pincer palladium complexes have been reported to decompose upon heating (*e.g.* 160 °C) to form active Pd nanoparticles. Most importantly, in this study the active Pd species were formed at relatively low temperature (*i.e.* 40 °C).

According to these kinetic investigations, the present C–P cross-coupling process presumably proceeds via a pathway as shown in Scheme 4 [40a,b]: i) complex **3** decomposes under the reaction conditions to form catalytically active Pd^0 nanoparticles, which can be oxidized to Pd^{2+} after reacting to aryl iodides; ii) deprotonation of the secondary phosphine-borane occurs in the presence of K_2CO_3 and the generated phosphorus anion attacks the palladium atom to afford Ar-Pd-PPh_2BH_3; iii) after reductive elimination, the desired tertiary phosphine-borane product forms with concomitant reduction of Pd^{2+} back to Pd^0.



Scheme 4. Proposed reaction mechanism for the C–P coupling process.

3. Conclusion

In summary, we have developed a series of novel phosphite palladium complexes **1**–**3** by using a straightforward synthetic route. Complexes **1** and **3** were characterized by X-ray crystal structure determinations. The application of phosphite PCP-pincer palladium complex **3** in C–P cross-coupling reactions was optimized with Ph-I and $Ph_2PhH(BH_3)$ as model substrates and complete conversion was obtained by using 10 mol% loading of **3** in MeCN at 40 °C in the presence of 2 equivalents of K_2CO_3. Following the optimized procedure, a series of tertiary phosphine-borane compounds were synthesized in promising to excellent yields with a very wide functional group tolerance and under mild conditions. The reaction profile and poisoning studies with metallic mercury and PPh_3 indicated the involvement of heterogeneous Pd^0 species as the actual catalyst. Pincer complex **3**, therefore, merely acts as a pre-catalyst which decomposes to generate catalytically active Pd nanoparticles that are able to catalyze C–P coupling reactions at very mild conditions.

4. Experimental section

4.1. General remarks

All reactions were performed under a dry N_2 atmosphere using standard Schlenk techniques. CH_2Cl_2, $ClCH_2CH_2Cl$, MeCN, and Et_3N were distilled over CaH_2 in a conventional heating bath before use. Toluene was freshly distilled over Na sand prior to use. PCl_3 was freshly distilled and stored under N_2 before use. All other reagents were purchased and used as received. ^1H NMR (^1H 400.0 MHz), ^{13}C NMR (^{13}C 100.6 MHz) and ^{31}P NMR (161.9 MHz) spectra were recorded at room temperature in $CDCl_3$ on a Varian 400 MHz INOVA spectrometer. Chemical shift values are reported in ppm (δ) relative to $(CH_3)_4Si$ (^1H and ^{13}C NMR) or a capillary containing 85% H_3PO_4 in D_2O ($^{31}P\{^1H\}$ NMR). Flash chromatography was performed using ACROS silica gel, 0.06–0.200 mm, pore diameter ca. 6 nm. MS measurements were carried out on an Applied Biosystems Voyager DE-STR MALDI-TOF MS. Elemental microanalyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a/d Ruhr, Germany.

4.2. General procedure for the preparation of phosphite ligands

2,2′-Biphenol (2 mmol, 0.3730 g) was azeotropically dried over toluene in vacuum three times and was suspended in freshly distilled PCl_3 (5 mL) at room temperature. The resulting mixture was heated at refluxing temperature for 2 h with vigorously stirring. During this procedure, HCl gas evolved and was trapped by a saturated aqueous NaOH solution. After cooling, the remaining PCl_3 was removed under reduced pressure and the trace amounts of PCl_3 were further azeotropically evaporated with dry toluene (3×5 mL). The resulting colorless oily product was directly used in the next step without purification. The oily product was redissolved in toluene (25 mL) and was added to a solution of azeotropically dried aryl alcohol (2 mmol of phenol; 1 mmol of resorcinol or 2,4-*tert*-butylbenzene-1,3-diol) in toluene (10 mL) at 0 °C (ice bath). To this mixture, a solution of Et_3N (0.31 mL, 2.2 mmol) in toluene (5 mL) was added drop wise over 5 min. The reaction mixture was then heated to 110 °C for 2 h under N_2. After cooling, the resulting white suspension mixture was filtered over a short plug of silica gel and the filter cake was washed with toluene (3×10 mL). The combined toluene layers were concentrated to dryness and a white solid was obtained. The analytic sample was obtained after further purification via flash chromatography with EtOAC/hexanes (1:1, v/v).

4.2.1. Ligand **4**

0.5430 g, 1.76 mmol; Yield: 88%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, $^3J_{H-H} = 1.5$ Hz, 1 H, BIPOL*H*, biphenyl-H2), 7.52 (d, $^3J_{H-H} = 1.5$ Hz, 1 H, BIPOL*H*, biphenyl-H3), 7.42–7.31 (m, 4 H, BIPOL*H*, biphenyl-H4, 4′ and H5, 5′ + 2 H, Ar*H*), 7.26–7.17 (m, 2 H, BIPOL*H*, biphenyl-H2′ and H3′ + 3H, Ph*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 Hz): δ 131.7, 130.5, 129.9, 129.8, 128.4, 127.1, 126.2, 125.3, 121.7, 120.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ 145.0 (s). Anal.Calcd for C, 70.13; H, 4.25; P, 10.05; found: C, 70.10; H, 4.27; P, 10.07.

4.2.2. Ligand **5**

0.5730 g, 0.88 mmol; Yield: 88%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52(m, 4H, BIPOL*H*, biphenyl-H2, 2′), 7.26–7.42(m, 12H, BIPOL*H*, biphenyl-H3, 3′, H4, 4′ and H5, 5′), 7.13 (s, 1H, Ar*H*), 7.04–7.07 (m, 1H, Ar*H*), 1.42 (s, 12H, *tBu*), 1.40 (s, 6H, *tBu*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 Hz): δ 135.4, 131.6, 129.9, 129.3, 127.2, 125.7, 122.4, 121.9, 121.7, 117.0, 35.0, 30.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ 145.0 (s). Anal. Calcd for C, 70.15; H, 5.58; P, 9.52; found: C, 70.17; H, 5.63; P, 9.49.

4.3. Complex **1**

A mixture of $[PdCl_2(NCMe)_2]$ (0.1 mmol, 0.0263 g) and ligand **4** (0.2 mmol, 0.062 g) in 10 mL dichloromethane was stirred at room temperature for 1 h. The reaction mixture was then concentrated under reduced pressure and a white solid was precipitated from the solution by the addition of hexanes. The solid was collected by centrifugation and further washed with 2 × 10 mL hexanes. The product was obtained as a fine white powder (0.0755 g, 0.095 mmol). Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.60 (m, 8H, BIPOL*H*, biphenyl-H2, 2′, H3, 3′), 7.40–7.45 (m, 8H, BIPOL*H*, biphenyl-H4, 4′, H5, 5′), 7.10 (d, $^3J_{H-H} = 7.2$ Hz, 6H, Ph*H*), 6.84–6.92 (m, 4H, Ph*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 Hz): δ 149.3, 148.0, 130.5, 130.3, 129.6, 129.3, 127.2, 126.5, 122.6, 121.6. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ 111.7 (s). Anal. Calcd for $C_{36}H_{26}Cl_2O_6P_2Pd$: C, 54.47; H, 3.30; P, 7.80; Pd, 13.41; found: C, 54.49; H, 3.37; P, 7.86; Pd, 13.45.

4.4. Complex **2**

A mixture of ligand **4** (0.1 mmol) and $PdCl_2$ (0.0180 g, 0.1 mmol) in 5 mL of toluene was heated at 110 °C for overnight under N_2. After cooling, the reaction mixture was filtered over a pad of Celite, all volatiles were removed under vacuum, and the residue crystallized from CH_2Cl_2/MeOH (1:9, v/v) to afford an orange solid (0.0450 g, 0.05 mmol). Yield: 50%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (br d, $^3J_{H-H} = 8$ Hz, 4H, Ph*H*), 7.35–7.50 (very br m, 16H, BIPOL*H*), 7.21–7.28 (very br s, 4H, Ph*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 Hz): δ 150.1, 148.0 (d, $J = 12$ Hz), 131.8, 130.4, 129.1, 129.0, 127.5, 127.2, 126.8, 122.6, 121.5 (d, $J = 4.5$ Hz), 116.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ 80.1 (br s) minor isomer, 81.4 (br s) major isomer. Anal. Calcd for $C_{36}H_{24}Cl_2O_6P_2Pd_2$: C, 48.14; H, 2.69; P, 6.90; Pd, 23.69 found: C, 48.22; H, 2.79; P, 6.88; Pd, 23.65.

4.5. Complex **3**

A mixture of the ligand **5** (0.0650 g, 0.1 mmol) and $[PdCl_2(NCMe)_2]$ (0.0264 g, 0.1 mmol) in 2 mL of 1,2-dichloroethane was treated with NEt_3 (14 μL, 0.10 mmol) and then heated at 80 °C for 2h. After cooling, the reaction mixture was filtered over a pad of Celite, all volatiles were removed under vacuum and the residue crystallized from CH_2Cl_2/pentane to afford a slightly orange solid (0.0515 g, 0.065 mmol). Yield: 65%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55(d, $^3J_{H-H} = 7.6$ Hz, 4H, BIPOL*H*, biphenyl-H2, 2′), 7.35–7.43 (m, 12H, BIPOL*H*, biphenyl-H3, 3′, H4, 4′ and H5, 5′), 7.22 (s, 1H, Ar*H*), 1.34 (s, 18H, *tBu*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 Hz): δ 152.6, 148.2, 137.1, 135.8, 132.6, 130.2 (d, $J = 23$ Hz), 129.5, 127.1, 125.6, 122.6, 35.0, 30.0. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ 146.2 (s). MS (MALDI-TOF): *m*/*z* calcd for $C_{38}H_{35}O_6P_2Pd$: 756.05 $[M-Cl]^+$; found: 756.04; Anal. Calcd for $C_{38}H_{35}ClO_6P_2Pd$: C, 57.66; H, 4.46; P, 7.83; Pd, 13.45; found: C, 57.71; H, 4.48; P, 7.79; Pd, 13.42.

4.6. General procedure of synthesis of tertiary phosphine-boranes

To a flame dried Schlenk tube, $Ph_2PH(BH_3)$ (20.0 mg, 0.1 mmol), aryl iodide (0.105 mmol), K_2CO_3 (28.0 mg, 0.2 mmol), complex **3** (7.9 mg, 0.01 mmol), and MeCN (1 mL) were added. This resulting mixture was warmed to 40 °C for 16 h under N_2. After cooling, water (2 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic layers were concentrated on a rotary evaporator and the residue was subjected to flash chromoatography (EtOAc/hexanes 3:7 (v/v)) to obtain the entitled tertiary phosphine-boranes as white solids. The spectral data of these compounds were identical to those reported in the literature (see Table 3, references).

4.7. General procedure of deprotection of tertiary phosphine-boranes

According to reported procedure [26], to a Schlenk tube equipped with condenser were added activated molecular sieves (250 mg, 4 Å), phosphine-boranes (0.05 mmol), THF (3.5 mL) and MeOH (1.5 mL). The reaction mixture was then refluxed for 96 h under N_2. After cooling, the reaction mixture was filtered through a pad of Celite and the filter cake was washed with THF (3 × 5 mL). All volatiles were removed on a rotary evaporator and the resultant waxy product was re-crystallized from MeOH/EtOAc at −30 °C to yield analytically pure samples as white solids. The spectral data of these compounds were identical to those reported in the literature (see Table 3).

4.8. Procedure of reaction profile study

A flame dried Schlenk tube equipped with a condenser was charged with $Ph_2PH(BH_3)$ (1 mmol), Ph-I (1.05 mmol), K_2CO_3 (2 mmol), complex **3** (0.1 mmol) and MeCN (4 mL). This reaction mixture was then warmed to 40 °C with vigorous stirring. Small aliquot (50 μL) was taken at alloted time and diluted in EtOAc (1 mL). The resulting organic mixture was washed with water (1 mL) and the aqueous layer was extracted with EtOAc (3 × 1 mL). The combined organic layers were dried over $MgSO_4$. Removal of all the volatiles under reduced pressure gave an oily orange mixure, which was redissovled in $CDCl_3$ and transfered into an NMR tube. The chemical conversion was determined by integration of corresponding ^{31}P resonances in the ^{31}P NMR spectra. Diethyl ethylphosphonate (10 μL) was added to the respective samples as an internal standard.

4.9. Procedure of poisoning tests

A flame dried Schlenk tube equipped with a condenser was charged with Ph_2PHBH_3 (0.1 mmol), Ph-I (0.105 mmol), K_2CO_3 (0.2 mmol), complex **3** (0.01 mmol) and MeCN (4 mL). This reaction mixture was warmed to 40 °C with vigorous stirring. Metallic mercury (300 equivalents) or PPh_3 (0.05 equivalent) were added to the reaction mixture at alloted time. Small aliquot (50 μL) was taken at alloted time and diluted in EtOAc (1 mL). The resulting organic mixture was washed with water (1 mL) and the aqueous layer was extracted with EtOAc (3 × 1 mL). The combined organic layers were dried over $MgSO_4$. Removal of all the volatiles under reduced pressure gave an oily orange mixture, which was dissolved

in $CDCl_3$ and transferred to an NMR tube. The chemical conversion was determined by integration of corresponding ^{31}P resonances in the ^{31}P NMR spectra. Diethyl ethylphosphonate (10 μL) was added to the respective samples as an internal standard.

4.10. X-ray crystal structure determinations

X-ray reflections were measured with Mo-K_α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer with rotating anode at a temperature of 150 K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. Integration of the intensities was performed with EvalCCD [41] and absorption correction with SADABS [42]. The structures were solved with Direct Methods (program SHELXS-97 [43] for complexes **1** and **3**; program SIR-97 [44] for complex **7**). Refinement was performed with SHELXL-97 [43] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps (complexes **1** and **7**) or introduced in calculated positions (complex **3**) and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program [45]. Further details are given in Table 1.

4.10.1. Complex *1*

With the matrix (1,0,−2/−1,0,0/0,1,0) the triclinic cell parameters can be transformed into a *pseudo*-monoclinic C-centered cell. The *a*-axis of the triclinic cell then becomes the *b*-axis of the pseudo-monoclinic cell. The two independent molecules in the triclinic cell are related by an approximate twofold rotation roughly about the *a*-axis. The reflection intensities only support a triclinic symmetry and there is no indication for twinning.

4.10.2. Complex *3*

Besides the ordered THF molecule, the crystal structure contains a large void (852.4 Å^3/unit cell), filled with disordered THF solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON [45], resulting in 60 electrons/unit cell.

Acknowledgements

We gratefully thank Utrecht University for financial support. This work was supported in part (ML, ALS) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO).

Appendix A. Supplementary material

CCDC 750414, 750415, and 750416 contain the supplementary crystallographic data for complex **1**, complex **3** and complex **7** in 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.

References

[1] For reviews: (a) D.S. Marynick, J. Am. Chem. Soc. 106 (1984) 4064–4065;
(b) P.B. Dias, M.E. Minas de Piedade, J.A. Martinho Simões, Coord. Chem. Rev. 135 (1994) 737–807;
(c) R.H. Crabtree, The Organometallic Chemistry of The Transition Metals, fourth ed. John Wiley & Sons, Inc., Hoboken, NJ, 2005;
(d) P.W.N.M. van Leeuwen, Homogeneous Catalysis. Kluwer Academic Publisher, Dordrecht, The Netherlands, 2003.
[2] For reviews: (a) S. Díez-González, S.P. Nolan, Acc. Chem. Res. 41 (2008) 349–358;
(b) J. Klosin, C.R. Landis, Acc. Chem. Res. 40 (2007) 1251–1259;
(c) S.A. Macgregor, Chem. Soc. Rev. (2007) 67–76;
(d) M.J. Burk, Acc. Chem. Res. 33 (2000) 363–372;
(e) W. Tang, X. Zhang, Chem. Rev. 103 (2003) 3029–3070;
(f) M. Diéguez, O. Pàmies, A. Ruiz, Y. Díaz, S. Castillón, C. Claver, Coord. Chem. Rev. 248 (2004) 2165–2192.
[3] For reviews: (a) M. Diéguez, O. Pàmies, C. Claver, Tetrahedron: Asymmetry 15 (2004) 2113–2122;
(b) K.N. Gavrilov, O.G. Bondarev, A.V. Korostylev, A.I. Polosukhin, V.N. Tsarev, N.E. Kadilnikov, S.E. Lyubimov, A.A. Shiryaev, S.V. Zheglov, H. Gais, V.A. Davankov, Chirality 15 (2003) S97–S103;
(c) M. Diéguez, C. Claver, O. Pàmies, Eur. J. Org. Chem. (2007) 4621–4634;
(d) P.C. Kamer, A. van Rooy, G.C. Schoemaker, P.W.N.M. van Leeuwen, Coord. Chem. Rev. 248 (2004) 2409–2424.
[4] For examples: (a) D.A. Albisson, R.B. Bedford, P.N. Scully, Tetrahedron Lett. 39 (1998) 9793–9796;
(b) R.B. Bedford, S.L. Welch, Chem. Commun. (2001) 129–130;
(c) R.B. Bedford, S.L. Hazelwood, D.A. Albisson, Organometallics 21 (2002) 2599–2600;
(d) R.B. Bedford, S.L. Hazelwood, M.E. Limmert, D.A. Albisson, S.M. Draper, P.N. Scully, S.J. Coles, M.B. Hursthouse, Chem.—Eur. J. 9 (2003) 3216–3227;
(e) R.B. Bedford, M. Betham, S.J. Coles, P.N. Horton, M. López-Sáez, Polyhedron 25 (2006) 1003–1010.
[5] For examples: (a) F. Miyazaki, K. Yamaguchi, M. Shibasaki, Tetrahedron Lett. 40 (1999) 7379–7383;
(b) R.A. Baber, R.B. Bedford, M. Betham, M.E. Blake, S.J. Coles, M.F. Haddow, M.B. Hursthouse, A.G. Orpen, L.T. Pilarski, P.G. Pringle, R.L. Wingad, Chem. Commun. (2006) 3880–3882;
(c) M. Rubio, A. Suárez, D. del Río, A. Galindo, E. Álvarez, A. Pizzano, Dalton Trans. (2007) 407–409;
(d) O.A. Wallner, V.J. Olsson, L. Eriksson, K.J. Szabó, Inorg. Chim. Acta 359 (2006) 1767–1772;
(e) J. Aydin, K.S. Kumar, M.J. Sayah, O.A. Wallner, K.J. Szabo, J. Org. Chem. 72 (2007) 4689–4697.
[6] For reviews: (a) E.J. Corey, X.M. Cheng, The Logic of Chemical Synthesis. John Wiley & Sons, New York, 1989;
(b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483;
(c) J.P. Corbet, G. Mignani, Chem. Rev. 106 (2006) 2651–2710;
(d) N. Marion, S.P. Nolan, Acc. Chem. Res. 41 (2008) 1440–1449;
(e) B.D. Sherry, A. Fürstner, Acc. Chem. Res. 41 (2008) 1500–1511;
(f) E. Negishi, Acc. Chem. Res. 15 (1982) 340–348;
(g) E.A.B. Kantchev, C.J. O'Brien, M.G. Organ, Angew. Chem., Int. Ed. 46 (2007) 2768–2813;
(h) S.R. Dubbaka, P. Vogel, Angew. Chem., Int. Ed. 44 (2005) 7674–7684.
[7] For reviews: (a) D.H. Valentine, J.H. Hillhouse, Synthesis 16 (2003) 2437–2460;
(b) D. Mingos, P. Michael, Mod. Coord. Chem. (2002) 69–78;
(c) B.L. Shaw, J. Organomet. Chem. 200 (1980) 307–318;
(d) T.B. Rauchfuss, In: L. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, 1983, p. 239–256
[8] For examples: (a) D.S. Glueck, Chem.—Eur. J. 14 (2008) 7108–7117;
(b) K.D. Berlin, G.B. Butler, Chem. Rev. 60 (1960) 243–260;
(c) A.L. Schwan, Chem. Soc. Rev. 4 (2004) 218–224;
(d) I.P. Beletskaya, A.V. Cheprakov, Coord. Chem. Rev. 248 (2004) 2337–2364;
(e) K.M. Pietrusiewicz, M. Zablocka, Chem. Rev. 94 (1994) 1375–1411;
(f) Y. Yoshinori, T. Imamoto, Heteroatom. Chem. 20 (1999) 227–248;
(g) D.S. Glueck, Synlett 17 (2007) 2627–2634;
(h) A. Grabulosa, J. Granell, G. Muller, Coord. Chem. Rev. 251 (2007) 25–90;
(i) J.J. Feng, X.F. Chen, M. Shi, W.L. Duan, J. Am. Chem. Soc. 132 (2010) 5562–5563.
[9] M. Murata, S.L. Buchwald, Tetrahedron 60 (2004) 7397–7403.
[10] C. Huang, X. Tang, H. Fu, Y. Jiang, Y. Zhao, J. Org. Chem. 71 (2006) 5020–5022.
[11] For examples: (a) K.Q. Yu, W. Sommer, M. Weck, C.W. Jones, J. Catal. 226 (2004) 101–110;
(b) K.Q. Yu, W. Sommer, J.M. Richardson, M. Weck, C.W. Jones, Adv. Synth. Catal. 347 (2005) 161–171;
(c) J.L. Bolliger, O. Blacque, C.M. Frech, Chem.—Eur. J. 14 (2008) 7969–7977.
[12] For examples: (a) W. Wei, Y. Qin, M. Luo, P. Xia, M.S. Wong, Organometallics 27 (2008) 2268–2272;
(b) B. Inećs, R. SanMartin, F. Churruca, E. Domićnguez, M.K. Urtiaga, M.I. Arriortua, Organometallics 27 (2008) 2833–2839;
(c) Q.L. Luo, S. Eibauer, O. Reiser, J. Mol. Catal. A: Chem. 268 (2007) 65–69;
(d) J.L. Bolliger, O. Blacque, C.M. Frech, Angew. Chem., Int. Ed. 46 (2007) 6514–6517.
[13] For examples: (a) E. Mas-Marzá, A.M. Segarra, C. Claver, E. Peris, Elena Fernandez, Tetrahedron Lett. 44 (2003) 6595–6599;
(b) F. Churruca, R. SanMartin, I. Tellitu, E. Domínguez, Synlett (2005) 3116–3117.
[14] A. Albinati, S. Affolter, P.S. Pregosin, Organometallics 9 (1990) 379–387.
[15] For phosphine PCP pincer: (a) D. Olsson, P. Nilsson, M. El Masnaouy, O.F. Wendt, Dalton Trans. 11 (2005) 1924–1929;
For phosphonite pincer: (b) J.-F. Gong, Y.-H. Zhang, M.P. Song, C. Xu, Organometallics 26 (2007) 6487–6492.
[16] R.B. Bedford, M. Betham, J.P.H. Charmant, M.F. Haddow, A.G. Orpen, L.T. Pilarski, S.J. Coles, M.B. Hursthouse, Organometallics 26 (2007) 6346–6353.
[17] For examples: (a) H. Lebel, S. Morin, V. Paquet, Org. Lett. 5 (2003) 2347–2349;
(b) R.J. Detz, S.A. Heras, R. de Gelder, P.W.N.M. van Leeuwen, H. Hiemstra, J.N.H. Reek, J.H. van Maarseveen, Org. Lett. 8 (2006) 3227–3230;

(c) H. Vallette, S. Pican, C. Boudou, J. Levillain, J.C. Plaquevent, A.C. Gaumont, Tetrahedron Lett. 47 (2006) 5191–5193;
(d) A. Gaumont, J.M. Brown, M.B. Hursthouse, S.J. Coles, Chem. Commun. (1999) 63–64;
(e) S. Pican, A. Gaumont, Chem. Commun. (2005) 2393–2395.
[18] (a) T. Imamoto, M. Matsuo, T. Nonomura, K. Kishikawa, M. Yanagawa, Heteroatom. Chem. 4 (1993) 475–486;
(b) T. Imamoto, T. Yoshizawa, K. Hirose, Y. Wada, H. Masuda, K. Yamaguchi, H. Seki, Hetereoatom. Chem. 6 (1995) 99–104.
[19] P.G. Schiemenz, Phosphorus, Sulfur Silicon Relat. Elem. 163 (2000) 185–202.
[20] H. Lebel, V. Paquet, J. Am. Chem. Soc. 126 (2004) 320–328.
[21] Y.C. Wang, C.W. Lai, F.Y. Kwong, W. Jia, K.S. Chan, Tetrahedron 60 (2004) 9433–9439.
[22] F.Y. Kwong, C.W. Lai, M. Yu, K.S. Chan, Tetrahedron 60 (2004) 5635–5645.
[23] D.V. Allen, D. Venkataraman, J. Org. Chem. 68 (2003) 4590–4593.
[24] H. Gulyás, Á. Szöllösy, P. Szabó, P. Halmos, J. Bakos, Eur. J. Org. Chem. (2003) 2775–2781.
[25] H. Gulyás, J. Benet-Buchholz, E.C. Escudero-Adan, Z. Freixa, P.W.N.M. van Leeuwen, Chem.—Eur. J. 13 (2007) 3424–3430.
[26] M. Schröder, K. Nozaki, T. Hiyama, Bull. Chem. Soc. Jpn. 77 (2004) 1931–1932.
[27] A. Köllhofer, H. Plenio, Chem.—Eur. J. 9 (2003) 1416–1425.
[28] F. Kwong, Y. Kin, S. Chan, Chem. Commun. (2000) 1069–1070.
[29] M. Nechab, E. Le Gall, M. Troupel, J.Y. Nédélec, J. Organomet. Chem. 691 (2006) 1809–1813.
[30] M.L. Williams, C.L. Noack, R.J. Saverin, P.C. Healy, Acta Crystallogr. E58 (2002) o419–o421.
[31] P. Machnitzki, T. Nickel, O. Stelzer, C. Landgrafe, Eur. J. Inorg. Chem. (1998) 1029–1034.
[32] C.M. Thomas, J.C. Peters, Inorg. Chem. 43 (2004) 8–10.
[33] X. Luo, H. Zhang, H. Duan, Q. Liu, L. Zhu, T. Zhang, A. Lei, Org. Lett. 9 (2007) 4571–4574.
[34] H. Christina, E. McFarlane, W. McFarlane, Polyhedron 7 (1988) 1875–1879.
[35] For acid-assistant deprotection process: (a) T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, J. Am. Chem. Soc. 120 (1998) 1635–1636;
(b) L. McKinstry, T. Livinghouse, Tetrahedron Lett. 35 (1994) 9319–9322.
[36] For base-assistant deprotection process: (a) T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, J. Am. Chem. Soc. 112 (1990) 5244–5252;
(b) H. Brisset, Y. Gourdel, P. Pellon, M. Le Corre, Tetrahedron Lett. 34 (1993) 4523–4526.
[37] (a) D.R. Anton, R.H. Crabtree, Organometallics 2 (1983) 855–859;
(b) P. Foley, R. DiCosimo, G.M. Whitesides, J. Am. Chem. Soc. 102 (1980) 6713–6725.
[38] (a) J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 198 (2003) 317–341;
(b) Y. Lin, R.G. Finke, Inorg. Chem. 33 (1994) 4891–4910;
(c) K.S. Weddle, J.D. Aiken, R.G. Finke, J. Am. Chem. Soc. 120 (1998) 5653–5666.
[39] B.M.J.M. Suijkerbuijk, S.D. Herreras Martínez, G. van Koten, R.J.M. Klein Gebbink, Organometallics 27 (2008) 534–542.
[40] (a) A.H.M. de Vries, J.M.C.A. Mulders, J.H.M. Mommers, H.J.W. Henderickx, J.G. de Vries, Org. Lett. 5 (2003) 3285–3288;
(b) T. Imamoto, T. Oshiki, T. Onozawa, M. Matsuo, T. Hikosaka, M. Yanagawa, Heteroatom. Chem. 3 (1992) 563–575.
[41] A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, J. Appl. Crystallogr. 36 (2003) 220–229.
[42] G.M. Sheldrick, SADABS: Area-Detector Absorption Correction, v2.10. Universität Göttingen, Germany, 1999.
[43] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112–122.
[44] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115–119.
[45] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.