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Reactions of benzyldiphenylphosphine with Pd(II) sources on silica gel

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ABSTRACT

Depending on the conditions used, reactions of benzyldiphenylphosphine (HL^1) with Na_2PdCl_4 on silica gel or with $Pd(OAc)_2$ on the same absorbent followed by treatment with LiCl provide one or more of the four compounds: the cyclopalladated binuclear complex $[(\mu\text{-Cl})PdL^1]_2$ (**1**), cis and trans isomers of the coordination complex $PdCl_2(HL^1)_2$ (**3**), the binuclear coordination complex $[(\mu\text{-Cl})PdCl(HL^1)]_2$ (**4**), and compound $PdCl_2(HL^1)_3$ (**5**). The 56% yield of complex **1** achieved using the reaction with Na_2PdCl_4 and NaOAc on SiO_2 is higher than that reported for the direct cyclopalladation of $PBnPh_2$ with $Pd(OAc)_2$ in AcOH. X-ray diffraction studies of the cyclopalladated dimer **1** and the coordination complex *cis*-**3** are reported.

1. Introduction

Due to growing environmental concerns, chemical synthesis using either no solvents or their reduced amount is an attractive and important trend [1]. Recently, mechanochemical approach has been recognized as a valuable method to perform reactions, including preparation of metal complexes, without solvents [2,3]. Microwave-assisted transformations using neat reactants are another way to lower consumption of chemicals [4]. One more approach is to perform reactions on silica gel and similar sorbents [5].

Recently, we reported a general method for cyclopalladation of *N*-containing preligands on SiO_2 with the use of solvents on the purification step only [6]. This method allowed preparation of the corresponding *C,N*-palladacycles in the yields comparable or even exceeding those reported for reactions performed under conventional conditions using solvents. Previously, Tune and Werner reported the conversion of $(\eta^5\text{-}C_5H_5)PdIP(O\text{-}ortho\text{-}Tol)_3$ to the cyclopalladated derivative $(\eta^5\text{-}C_5H_5)Pd[P(OC_6H_3\text{-}ortho\text{-}Me)(O\text{-}ortho\text{-}Tol)_2]$ during chromatography on SiO_2 [7]. To the best of our knowledge, there have been no other studies related to the use of *P*-containing preligands in C–H bond activation on this or similar absorbents.

Pursuing our interest in chemistry of cyclopalladated and Pd(II) coordination complexes, we examined reactions of commercially available benzyldiphenylphosphine, $PBnPh_2$ (HL^1), with $Pd(OAc)_2$ and Na_2PdCl_4 on SiO_2. Tertiary monodentate phosphines are capable of reacting with Pd(II) sources to give a variety of compounds. In particular, $PBnPh_2$ can form at least five Pd(II) complexes, **1**–**5**; four of them, **1**–**4,** have been reported. Two of the known compounds, **1** [8–12] and **2** [12], contain a five-membered palladacycle with a C–Pd bond, while complexes **3** [13–19] and **4** [9,20] have only dative P–Pd bonds (Chart 1). In general, preparation and use of cyclopalladated [21,22] and Pd(II) coordination complexes of phosphines have been subjects of considerable interest for a few decades. The main application of these complexes is in catalysis [23], although they have been also used as precursors for synthesis of valuable organic compounds [24] and other Pd complexes [25,26]. Therefore, the importance of phosphine-derived Pd(II) complexes as well as a growing demand for green approaches in synthesis have warranted our study of reactions of $PBnPh_2$ with Pd(II) sources on SiO_2.

2. Results and discussions

2.1. Reactions of $PBnPh_2$ with $Pd(OAc)_2$ and Na_2PdCl_4

Two Pd(II) sources, $Pd(OAc)_2$ and Na_2PdCl_4, were tested in reactions with $PBnPh_2$ on SiO_2 (Scheme 1 and Table 1). Because the target product was the cyclopalladated complex **1**, a 1:1 ratio of Pd per ligand was used in all experiments unless indicated otherwise. Two sizes of SiO_2 were used, 100–230 and 230–400 mesh. In some cases, the weak base NaOAc was added to promote cyclopalladation. In the experiments with $Pd(OAc)_2$, reactions on SiO_2 were followed by treatment with LiCl. Depending on the reaction conditions used, four different compounds were formed. One of the

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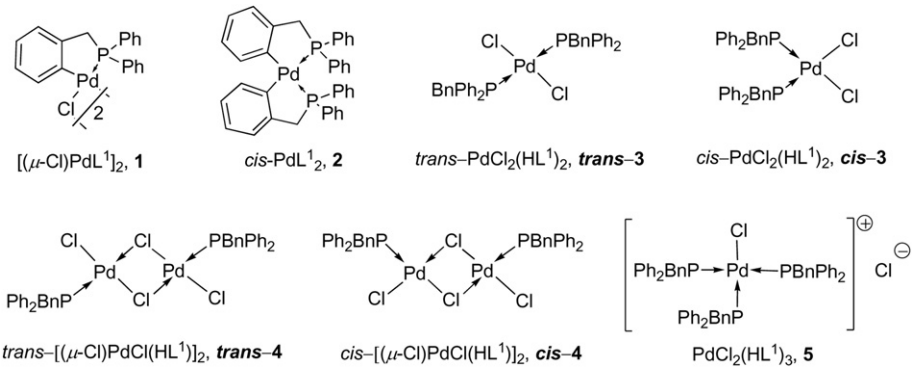
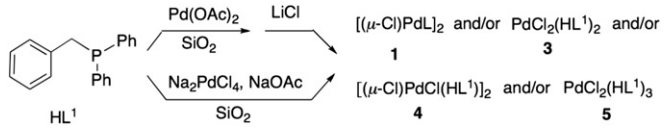


Chart 1. Pd(II) complexes with $PBnPh_2$ as a ligand or preligand.



Scheme 1.

complexes was the target cyclopalladated dimer **1**. The remaining three complexes, **3**–**5**, were coordination complexes with different ratios of Pd and $PBnPh_2$.

Reactions of $PBnPh_2$ with $Pd(OAc)_2$ at 50 °C selectively provided the dinuclear coordination complex $[(\mu\text{-Cl})PdCl(HL^1)]_2$, **4**, with yields up to 90% (entries 1 and 2). Attempts at performing similar experiments at higher temperatures resulted in the formation of Pd black. It is known that weak bases, particularly NaOAc, promote cyclopalladation [27]. Addition of NaOAc to the $PBnPh_2$–$Pd(OAc)_2$ reaction mixture, as well as increasing the temperature to 85 °C, resulted in the formation of the dinuclear cyclopalladated complex $[(\mu\text{-Cl})PdL^1]_2$, **1**, in 14% yield (entry 3).

Na_2PdCl_4 is known to be a less effective palladating agent than $Pd(OAc)_2$ and is commonly used in a combination with NaOAc [28]. Reactions of $PBnPh_2$ with Na_2PdCl_4 without a base at 40–85 °C provided, at best, only trace amounts of the cyclopalladated complex **1** (entries 4–8). The major product of these reactions was the coordination complex $PdCl_2(HL^1)_2$, **3**. Addition of NaOAc and increasing the temperature while shortening the reaction time allowed for improvement in the yield of the cyclopalladated complex up to 56% (entries 10–13).

Two sizes of SiO_2 were used in the study, 100–230 and 230–400 mesh (particles with the diameter of 63–149 and 37–63 μm, respectively). In the experiments with $Pd(OAc)_2$ with or without NaOAc, there was no significant SiO_2 size effect on the product yields or the product compositions. However, experiments at 120 °C with SiO_2 of the larger size, 100–230 mesh, provided a much higher yield of CPC **1** than those with the smaller size (entries 13 and 14).

To prove that cyclopalladation of $PBnPh_2$ does not occur with Na_2PdCl_4 without SiO_2, two experiments were performed. In the first experiment, a 1:1:1 mixture of $PBnPh_2$, Na_2PdCl_4 and NaOAc was heated at 85 °C for 5 h (entry 9, *cf.* entry 10). The $^{31}P\{^1H\}$ NMR spectrum of the mixture showed the presence of the phosphine oxide, *cis*-**3** and *trans*-**3** with no traces of complexes **1**, **4** and **5**. In the other experiment, a 1:1 mixture of $PBnPh_2$ and Na_2PdCl_4 was heated at 120 °C for 1 h (entry 15). While the use of these conditions on SiO_2 resulted in the formation of the cyclopalladated complex in a good yield (entry 13), the reaction without the absorbent provided only complex **3** in 9% yield.

In all experiments, acetone was used at rt to remove complexes from SiO_2. To prove that acetone does not affect the outcome of the reactions, a 1:1:1 mixture of **1**, Na_2PdCl_4 and NaOAc was mixed with SiO_2 at rt followed by addition of acetone. After filtration, the acetone solution was analyzed for the presence of complexes **1** and **2**–**5**. The $^{31}P\{^1H\}$ NMR spectrum contained signals of *cis*- and *trans*-**3**, the unreacted ligand and the corresponding oxide. No signals of the cyclopalladated complex **1** and compounds **4** and **5** were observed. After purification, complex **3** was isolated in 19% yield. Mixing ligand **1** with Na_2PdCl_4 in a 1:1 ratio on silica gel followed

Table 1
Reactions of $PBnPh_2$ with $Pd(OAc)_2$ and Na_2PdCl_4 on silica gel.[a]

Entry	Pd(II) source	Base	SiO_2 size, mesh	*T*, °C	Time, h	Yield of **1**, %	Yield of **3**, %	Yield of **4**, %	Yield of **5**, %
1	$Pd(OAc)_2$		230–400[c]	50	72			90	
2	$Pd(OAc)_2$		100–230[c]	50	168			69	
3	$Pd(OAc)_2$	NaOAc	100–230	85	168	14		6	
4	Na_2PdCl_4		100–230[c]	20	1		83		
5	Na_2PdCl_4		230–400	40	1		77	12	
6	Na_2PdCl_4		100–230	40	1		87	8	
7	Na_2PdCl_4		230–400	85	5		60		20
8	Na_2PdCl_4		100–230	85	5	3[b]	68	11[b]	
9	Na_2PdCl_4		None	85	5		9		
10	Na_2PdCl_4	NaOAc	230–400	40	72	13		31	51
11	Na_2PdCl_4	NaOAc	100–230	85	18	17			39
12	Na_2PdCl_4	NaOAc	100–230	85	168	21		13	42
13	Na_2PdCl_4	NaOAc	100–230	120	1	56			42
14	Na_2PdCl_4	NaOAc	230–400	120	1	9		34	25
15	Na_2PdCl_4	NaOAc	None	120	1		12		

[a] Yields are given for isolated compounds unless indicated otherwise; 750 mg of SiO_2 per 1 mmol of $PBnPh_2$ was used unless indicated otherwise.
[b] The values were estimated using ^1H NMR spectra.
[c] 375 mg of SiO_2 per 1 mmol of $PBnPh_2$ were used.

by addition of acetone also resulted in the formation of complex **3** only (11% yield after purification). Application of $Pd(OAc)_2$ instead of Na_2PdCl_4 in a similar experiment followed by addition of LiCl provided a complex mixture with no signals of complexes **1** and **3**–**5**.

Thermal stability of the complexes was also studied. Compound **1** was stable on the 100–230 and 230–400 mesh SiO_2 at 120 °C for at least 5 h. Complex **3** did not change its structure at 85 °C for at least 5 h. Compound **4** was stable at 50 °C for at least 24 h.

2.2. Cyclopalladated complex $(PdClL^1)_2$, **1**

Previously, complex **1** and its μ-OAc and μ-Br analogs were synthesized by three different methods. Hiraki et al. obtained **1** in 19% yield by cyclopalladation of $PBnPh_2$ by $Pd(OAc)_2$ in MeOH under reflux for 3 h [8]. Abicht and Issleib prepared compound **1** by reacting the spiro complex **2** with $PdCl_2$•$2Et_2S$ in 92% [12]. The same authors converted complex **2** to the μ-Br analog of **1** in 86% using $HgBr_2$ [12]. Ryabov et al. reported preparation of **1** in 21% yield using the transmetalation reaction between $PBnPh_2$ and the cyclopalladated complex $[(\mu\text{-Cl})PdL^2]_2$ ($HL^2 = N,N$-dimethylbenzylamine) in $CHCl_3$–AcOH at rt [11]. Applying different conditions (PhMe–CF_3CO_2H, reflux) to the same reaction, Pfeffer's group increased the yield of the crude complex **1** to 90% [10]. In our hands, this procedure provided 52% of **1** after dry-flash chromatography using hexane and CH_2Cl_2 as eluents. In the present study, the best yield of 56% was obtained when a mixture of the phosphine, Na_2PdCl_4 and NaOAc on 100–230 mesh silica gel was stirred for 1 h at 120 °C.

Surprisingly, no structure confirmation has been reported for the cyclopalladated complex except for the IR frequency of the C=O bond of the acetone adduct **1**•1/2Me_2C=O [8]. In the present study, the structure of complex **1** was supported by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of the compound contained two partly overlapping singlets in ca. 2:3 ratio that suggests the presence of two isomers, syn and anti. This type of the isomerism is well known for μ-Cl dimeric cyclopalladated complexes [29]. The X-ray study of complex **1** unambiguously confirmed its anti geometry in the solid form (see below).

2.3. Coordination complexes cis-$PdCl_2(HL^1)_2$, cis-3, and trans-$PdCl_2(HL)_2$, trans-**3**

The coordination complex **3** is usually synthesized by reacting $PBnPh_2$ with $PdCl_2(NCPh)_2$ or $PdCl_2(NCMe)_2$ in CH_2Cl_2 or another solvent [13,14,17]. In solution this complex exists as a mixture of two geometrical isomers, which undergo reversible thermal isomerization [17].

In our experiments on SiO_2, complex **3** was formed in many reactions in spite of using a 1:1 ratio of Pd per ligand. The obtained ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data were in good agreement with the previously reported data [16,17,19,30]. $^{31}P\{^1H\}$ NMR spectra of the isolated samples in $CDCl_3$ contained either one signal assigned to the thermodynamically more stable [15,31] cis form or two signals belonging to *cis*-**3** and *trans*-**3**. Similar data have been reported for other Pd(II) coordination complexes with phosphorus-containing ligands [32–35].

2.4. Dinuclear coordination complex $[(\mu\text{-Cl})PdCl(HL^1)]_2$, **4**

Dinuclear coordination complexes of phosphorus-containing ligands are rather common [36–44] and are usually synthesized by reacting a Pd(II) source with an appropriate ligand in a 1:1 ratio, i.e. using the same stoichiometry of the reagents as in cyclopalladation. In the case of bulky phosphines, the formation of dinuclear coordination complexes is more favored than their mononuclear analogs. It is noteworthy that ligand's steric bulk is also known to be an important factor promoting cyclopalladation [45]. Interestingly, very bulky phosphines are also capable of reacting with $PdCl_2$ to yield trinuclear coordination complexes, $[(HL)ClPd(\mu\text{-Cl})_2Pd(\mu\text{-Cl})_2PdCl(HL)]$, instead of dinuclear coordination or cyclopalladated complexes [46].

In our study, compound **4** was isolated in the highest yield of 90% in the experiment with $Pd(OAc)_2$ after treatment of the reaction mixture with LiCl (entry 1). The complex provided one signal in the $^{31}P\{^1H\}$ NMR spectrum, suggesting the presence of only one isomer. The conformation of the structure of complex **4** was obtained by X-ray analysis. The results matched the recently published data for the crystal structure of *trans*-$[(\mu\text{-Cl})PdCl(HL^1)]_2$ [20].

2.5. Coordination complex $PdCl_2(HL^1)_3$, **5**

Complexes of this type are relatively rare and unknown for $PBnPh_2$. For some phosphines, formation of complexes $PdCl_2(HL)_3$ was observed using $^{31}P\{^1H\}$ NMR spectroscopy by adding 1 equiv. of phosphine HL to a solution of $PdCl_2(HL)_2$ [48,49]. The reported spectrum of $PdCl_2(PMe_3)_3$ at −90 °C appeared as an AB_2 spin system, δ −6.6 and −5.3 ppm (CD_2Cl_2, relative to 62.5% H_3PO_4) [48], while the spectrum of $PdCl_2(PPhMe_2)_3$ at −60 °C was described as a sharp doublet and a sharp triplet in a 2:1 ratio at δ 48.6 and 45.2 ppm ($CDCl_3$, 85% H_3PO_4). Another reported pentacoordinate complex, $PdCl_2(PBnMe_2)_3$, was obtained as white crystals by refluxing a 1:2 ratio of Li_2PdCl_4 and $PBnMe_2$ in MeOH and converted to $[PdCl(PBnMe_2)_3]BF_4$ after treatment with $NaBF_4$ [50].

The elemental analysis of compound **5** suggested that its composition is $PdCl_2(HL^1)_3$. In order to get more experimental data to support the proposed structure of complex **5**, $^{31}P\{^1H\}$ NMR spectra of this compounds were taken at rt as well as at lower temperatures. The $^{31}P\{^1H\}$ NMR signal of **5** observed at −88 °C had a shoulder suggesting non-equivalency of the phosphine ligands in the compound. As it was reported for $Pd(PPhMe_2)_3Cl_2$ [40], the chemical shift of complex **5** is between those of *cis*- and *trans*-**3** (Fig. 1).

Attempts to grow crystals of complex **5** failed due to its decomposition that provided the coordination complex **3** and $BnPh_2P=O$. The structure of the latter was confirmed by X-ray crystallographic data.

2.6. X-ray structural analysis of complexes **1** and cis-**3**

The cyclopalladated structure of complex **1** was unambiguously confirmed by the X-ray diffraction study (Fig. 2). The molecular

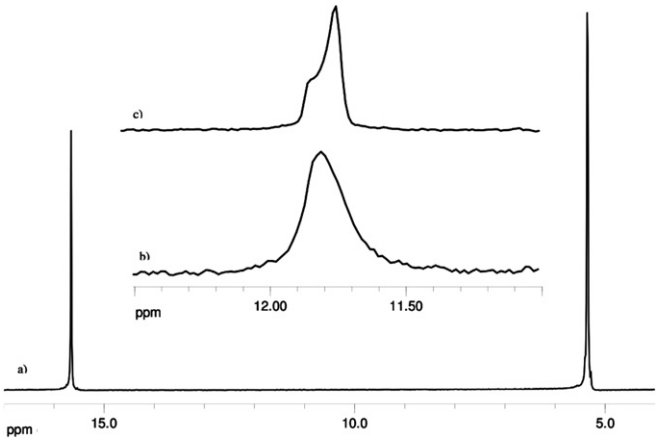


Fig. 1. $^{31}P\{^1H\}$ NMR spectra of: (a) a mixture of *cis*- and *trans*-**3** in $CDCl_3$ at rt, (b) complex **5** in $CDCl_3$ at rt, and (c) complex **5** at −88 °C in d_6-acetone.

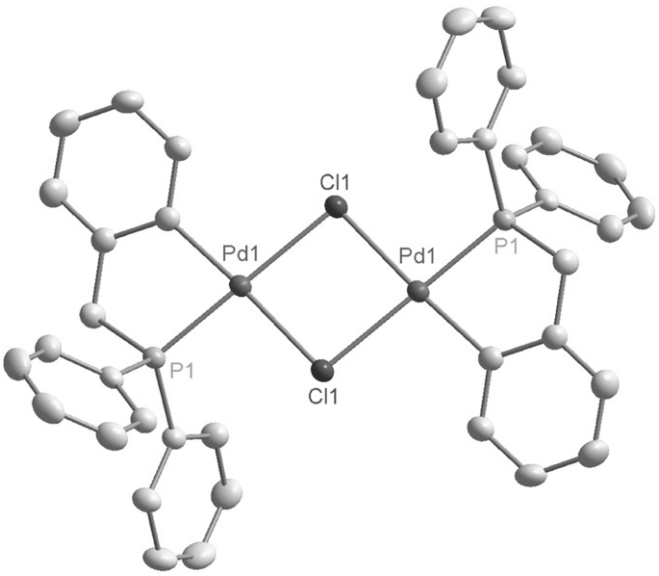


Fig. 2. The molecular structure of complex **1**.

structure of dimer **1** revealed its *anti* configuration with two P atoms trans to each other. The same geometry was found in structures of other chloro-bridged dimers with five-membered phosphapalladacycles, particularly those with the (sp^2)C–Pd bond, **I**–**IV** (Chart 2) [24,51–53]. The structure of complex **1** is a CH_2Cl_2 solvate and consists of two halves, which have minimal differences in the parameters. Both palladium centers are in distorted square-planar geometry with the dihedral angle of 3.9° between the {P(1)–Pd(1)–C(1)} and {C(1)–Pd(1)–Cl(1A)} planes. For comparison, the value of this angle in complexes (*R,R*)-**I**, (*S,S*)-**I**, **II** and **III** is 9.8, 9.7, 23.7, 2.6°, respectively. The $\{Pd_2Cl_2\}$ ring in the structure of dimer **1** was completely flat: the value of the {Pd(1)–Cl(1)–Cl(1A)–Pd(1A)} dihedral angle is 180.0°. In contrast, complexes (*R,R*)-**I** and (*S,S*)-**I** with the PPh_2 moiety exhibited a very significant bent of the $\{Pd_2Cl_2\}$ fragment, 52.8 and 51.1°, respectively. Compound **IV** with the PBu^t_2 group had a less significant bent of 28.8°, while reported halogen-bridged (sp^3)C,P-cyclopalladated complexes exhibited the practically flat $\{Pd_2Hal_2\}$ fragment [54,55] even in the structure with two mesityl substituents at the donor P atom [56].

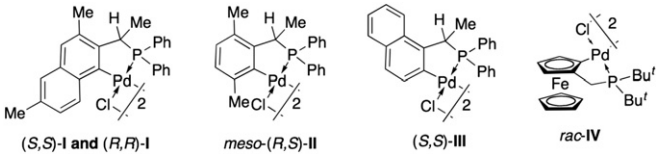


Chart 2. Cyclopalladated chloro-bridged dimeric complexes derived from tertiary phosphines with known molecular structures.

The length of the Pd–P bond found in **1**, 2.1953(5) Å, is within the range of 2.186–2.217 Å reported for the complexes (*R,R*)-**I**, (*S,S*)-**I**, **II** and **III** with the PPh_2 moiety and shorter than in related complexes with the Pd–PBu^t_2 fragment [53,55]. The Pd–C bond length of 2.009(2) Å in **1** is slightly shorter than those reported for their PPh_2 analogs **I**–**III**, 2.019–2.052 Å, but a little bit longer than in **IV**, 1.981 and 1.989 Å. Two Pd–Cl bonds in each half of the structure are slightly different, 2.4267(5) and 2.4393(5) Å. These values are typical for other chloro-bridged phosphapalladacycles [24,51–53]. The length difference for the Pd–Cl bonds in **1**, 0.0126 Å, is greater than that observed in **I**–**III**, 0.001–0.005 Å; however, the difference is smaller than that in **IV**, 0.020 Å and significantly smaller than in palladacycles with the (sp^3)C donor atom, in which the Pd–Cl bond trans to the P atom is significantly shorter, up to 0.088 Å [56]. These observations suggest similar trans influence of the (sp^2)C atom and the heteroatom in the PPh_2 fragment in complexes **1** and **I**–**IV** and a greater trans influence of the (sp^3)C donor atom compared to its sp^2-hybridized counterpart [22].

The extent of the palladacycle's puckering in complex **1** was estimated by calculating the average intrachelate torsion angle. The obtained value of 17.2° is less than that found in (*S,S*)-**I,** (*R,R*)-**I** and **II**, 27.0, 27.2 and 31.4° [24,51], but typical for other palladacycles derived from arylphosphines [53].

The X-ray study of complex **3** revealed its cis geometry in the solid state (Fig. 3). The structure is a $CHCl_3$ solvate. The X-ray diffraction study of complex **4** was also performed and revealed its trans geometry in the solid state. Because the molecular structure of *trans*-$\{(\mu\text{-Cl})PdCl(HL^1)\}_2$ is known [20], our data for complex **4** will be used here only for comparison with other Pd(II) complexes of $PBnPh_2$ (Table 2).

The majority of available X-ray studies of the coordination complexes $PdCl_2(HL)_2$, where HL is a tertiary phosphine or a similar *P*-donor ligand, report their trans geometry in the solid state [37–42,46,57–59]. X-ray studies of the *cis*-$PdCl_2(HL)_2$ complexes with *P*-donor ligands are more rare and include derivatives of PMe_2Ph [60], PMe_2(2-Py) [61], PPh(2-Py)$_2$ [62], PPh_2(OEt) [63], $P(OPh)_3$ [64] and a *P*-monodentate phosphoramidite [65].

The structure of *cis*-**3** showed a distorted square-planar environment of the Pd atom. The P–Pd–P angle was more obtuse than Cl–Pd–Cl by 10.76°. Such a difference is typical for *cis*-$PdCl_2(HL)_2$ complexes with P-donor ligands [60–62,64]; the only exception is *cis*-$PdCl_2[PPh_2(OEt)]_2$, in which the Cl–Pd–Cl angle was greater than P–Pd–P by 1.29° [63]. Parameters of two $PBnPh_2$ ligands as well as two Pd–Cl bond lengths in *cis*-**3** were slightly different, e.g. one Pd–P bond was shorter that the other by 0.0047 Å. For comparison, each of two structures, *cis*-$PdCl_2[PPh_2(OEt)]_2$ and *cis*-$PdCl_2(PMe_2Ph)_2$, displayed identical Pd–P and Pd–Cl bonds, while the difference in two Pd–P bonds in *cis*-$PdCl_2[PPh_2(2\text{-py})]_2$ was 0.0100 Å [60,62,63]. The Pd–P and Pd–Cl bond lengths in *cis*-**3** are within the range reported for other *cis*-$PdCl_2(HL)_2$ complexes [60–64].

It is known that both types of coordination complexes, $PdCl_2(HL)_2$ and $[(\mu\text{-Cl})PdCl(HL)]_2$, can, in some cases, be converted to the corresponding cyclopalladated complexes [52,66–68]. Coordination of the Pd atom to the heteroatom of HL is recognized as in initial step of metallation. As one can expect, after palladation, the Pd–P bond in **1** became significantly shorter than in the coordination complexes: by 0.0746 Å compared to **3**, and by 0.0265 Å

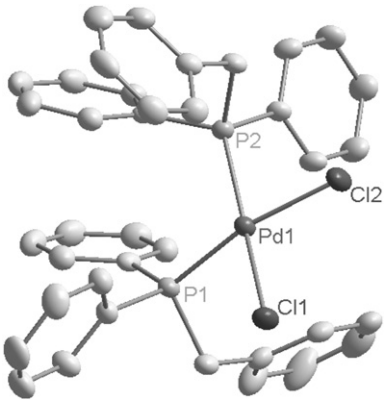


Fig. 3. Molecular structure of *cis*-**3**. The $CHCl_3$ solvate molecule was omitted for clarity.

Table 2
Selected geometric parameters for complexes *trans*-**1**, *cis*-**3** and *trans*-**4**.

Complex	Bond Length, Å				Angle, °		
	Pd–P	Pd–μ-Cl	Pd–C	P–CH_2	P–Pd–C	Cl–Pd–Cl	P–Pd–Cl
trans-**1**	2.1953(3)	2.4393(5)[a] 2.4267(5)[b]	2.009(2)	1.832(2)	82.04(6)	97.75(6)[d]	178.283(18) 95.104(19)
cis-**3**	2.2652(9) 2.2699(9)	2.3509(9) 2.3252(9)		1.864(4) 1.844(4)		89.15(3)	86.96(3) 85.47(3)
trans-**4**		2.4122(5)[a] 2.3153(4)[b] 2.2734(4)[c]		1.8325(17)		85.538(16)[d] 91.371(17) 176.452(15)	176.349(15)[a] 95.630(16)[b] 87.350(17)[c]

[a] Data for the μ-Cl–Pd trans to the Pd–P bond.
[b] Data for the μ-Cl–Pd cis to the Pd–P bond.
[c] Data for the Cl–Pd cis to the Pd–P bond.
[d] Data for the μ-Cl–Pd–μ-Cl angle.

compared to **4**. The $Ph_2P–CH_2$ bond in **1** was compressed as well: by 0.032 and 0.012 Å compared to two corresponding bonds in *cis*-**3** and by 0.009 Å compared to **4**. The {Pd(1)–Cl(1)–Cl(1A)–Pd(1A)} dihedral angle in **4** was the same as in complex **1**, 180.0°

3. Conclusions

Depending on the conditions used, reactions of $BnPh_2P$ with Pd(II) sources on silica gel provide one or more of the following compounds: the cyclopalladated binuclear complex **1** and three different types of coordination complexes **3**–**5**. The formation of the cyclopalladated complex **1** is the first example of the solvent-free phosphine C–H bond activation on silica gel. This method is expected to be useful for cyclopalladation of other *P*-containing preligands.

4. Experimental

4.1. General methods and materials

All reactions were carried out in a glove box using the atmosphere of N_2. Purifications by preparative thin-layer chromatography (TLC) were carried out using 200 × 250 mm glass plates with an unfixed layer of Natland or Merck silica gel 60 (230 mesh). Analytical TLC was performed on Whatman silica gel 60 (F_{254}) 250 *m*m precoated plates. Compounds were visualized on TLC plates using UV light (254 nm) and/or iodine stain. ^1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz) and $^{31}P\{^1H\}$ (202 MHz) as well as DEPT, COSY and HMQC spectra were recorded on a Bruker AVANCE 500 NMR spectrometer. Chemical shifts, δ, are reported in ppm with $SiMe_4$ as an internal standard (^1H and ^{13}C) or $P(OEt)_3$ as an external standard (^{31}P). Spin-spin coupling constants, *J*, are given in Hz. Spectra of all complexes were recorded in $CDCl_3$. Hexane, toluene and CH_2Cl_2 were distilled over CaH_2. Acetone was distilled over $KMnO_4$. $PBnPh_2$ and Na_2PdCl_4 were purchased from Sigma-Aldrich Co. and used without purification. $Pd(OAc)_2$ was also purchased from Sigma-Aldrich Co.; prior to use, the compound was dissolved in hot benzene, the solution was filtered and then the solvent was removed under reduced pressure.

Di-μ-chlorobis-{2-[(diphenylphosphino)methyl]phenyl-*C*,*P*} dipalladium(II) (1). *Method 1 (preparation in solvent)* [11]. In a glove box, $PBnPh_2$ (0.2300 g, 0.8324 mmol) was placed into an Ar-filled 50-mL Schlenk flask, then di-(μ-chloro)bis-{[2-(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) (0.2138 g, 0.3872 mmol) was added followed by abs. toluene (6 mL). In several minutes, CF_3COOH (0.07 mL) was added to the flask through the septum. The reaction mixture was refluxed for 2 h under the Ar atmosphere. After cooling the mixture to rt, toluene was removed using a rotavapor. Purification of the residue using dry-flash chromatography with the hexane-CH_2Cl_2 eluent system afforded cyclopalladated complex **1** (0.201 g, 52% yield) as a very light yellow solid. *Method 2 (preparation on SiO_2)*. In a glove box, $PBnPh_2$ (0.0340 g, 0.123 mmol) was placed into a small flask. Then Na_2PdCl_4 (0.0276 g, 0.123 mmol), SiO_2 (100–230 mesh, 0.0923 g; 0.750 g of SiO_2 per 1.00 mmol of the preligand) and NaOAc (0.0100 g, 0.123 mmol) were added to the flask and the mixture was vigorously stirred using a spatula for 1 min. The flask was topped with cotton and placed in a preheated (120 °C) sand bath to stir. After 1 h, the reaction mixture was transferred into a glass filter and the crude dimer was washed from SiO_2 with acetone (5 × 10 mL). The solution was placed on a rotavapor to remove acetone. The solid residue was dissolved in a minimal volume of CH_2Cl_2 and purified using preparative TLC (silica gel, CH_2Cl_2). Two compounds were isolated: complex **1** as a light yellow solid in 56% yield and complex **4** as an off-white powder in 42% yield. Crystals of **1** suitable for X-ray analysis were obtained using crystallization from CH_2Cl_2 at −5 °C. R_f 0.69 (CH_2Cl_2), m.p. 197–201 °C (decomp.; lit. data [8,12]: 198 and 248 °C). ^1H NMR: 3.81 (d, 2H, $^2J_{HH} = 15$, CH_2), 6.90 (br. s, 2H, H(4,5) of C_6H_4Pd), 7.01 (d, 1H, $^3J_{HH} = 7.9$, H(6) of C_6H_4Pd), 7.26 (d, $^3J_{HH} = 7.9$, 1H, H(3) of C_6H_4Pd); 7.35 (m, 5H, *p*- and *m*-H of PPh_2), 7.56 (br. s, 1H, *p*-H of PPh), 7.64 and 7.74 (br. s, 4H, *o*-H of PPh_2); $^{31}P\{^1H\}$ NMR: 41.40 and 41.43 in 2:3 ratio (lit. data [12]: δ 55.95 ppm in $CDCl_3$/d_6-DMSO relative to 85% H_3PO_4). The $^{13}C\{^1H\}$ NMR data were not obtained due to a poor solubility of the complex. Anal. Calcd for $C_{38}H_{32}Cl_2P_2Pd_2{\cdot}CHCl_3$: C, 49.11; H, 3.49%. Found: C, 48.82; H, 3.48%.

Dichlorobis(benzyldiphenylphosphine)palladium(II) (3). In a glove box, $PBnPh_2$ (0.0490 g, 0.1773 mmol) was placed in a small flask. Then Na_2PdCl_4 (0.0522 g, 0.177 mmol) and SiO_2 (100–230 mesh, 0.692 g; 0.375 g per 1.00 mmol of the preligand) were added and vigorously mixed using a spatula for 1 min. The flask was topped with cotton and stirred at rt for 1 h. Next, the reaction mixture was transferred into a glass filter and the crude product was washed from SiO_2 with acetone (5 × 10 mL). The solvent was removed using a rotavapor, the dry residue was dissolved in a minimal volume of CH_2Cl_2 and the product was purified using preparative TLC (silica gel, CH_2Cl_2). A mixture of *cis*- and *trans*-**3** was isolated as a bright yellow solid in 83% yield (0.0534 g). Sample crystallization from a $CDCl_3$ solution at rt afforded X-ray suitable crystals of *cis*-**3**. R_f 0.8 (*cis*-**3**) and 0.3 (*trans*-**3**, CH_2Cl_2), m.p. 200–201 °C (lit. data [15,30]: 205–207 and 182–193 °C). ^1H NMR (a mixture of *cis*-* and *trans*-**3**): 3.95 and 4.12* (t and d, 2H, $^2J_{HP} = 4$ and $^2J_{HP} = 12$, CH_2), 6.98–7.16 (m, 5H, PBn), 7.32 (m, 4H, *m*-H of PPh), 7.42 (m, 2H, *p*-H of PPh), 7.50 (m, 4H, *o*-H of PPh); $^{31}P\{^1H\}$ NMR (a mixture of *cis*-* and *trans*-**3**): 15.64* and 5.27 (lit. data for *cis*-**3**: 29.6 [19], 30.27 [17] and 30.29 [30]; for *trans*-**3**: 20.06 [16,17] and 20.03 [30]; all lit. data are for $CDCl_3$ solutions relative to 85% H_3PO_4); $^{13}C\{^1H\}$ NMR (a mixture of *cis*-* and *trans*-**3**): 32.2

(t, $^1J_{CP} = 12$, CH_2) and 39.3* (d, $^1J_{CP} = 12$, CH_2), 126.6–134.1 (PBn and PPh signals). Anal. Calcd for $C_{38}H_{34}Cl_2P_2Pd{\bullet}CDCl_3$: C, 55.09; H, 4.27%. Found: C, 54.92; H, 4.16%.

Dichlorodi-μ-chlorobis(benzyldiphenylphosphine)dipalladium(II) (4). *Method 1 (preparation in solvent).* In a glove box, $PBnPh_2$ (0.0310 g, 0.112 mmol) was placed into an Ar-filled 10 mL Schlenk flask. Then Na_2PdCl_4 (0.0330 g, 0.112 mmol) was added to the flask along with abs. toluene (15 mL). The suspension was stirred for 2 days at rt under the Ar atmosphere. The solvent was removed and the crude product was purified using dry-flash chromatography with acetone and CH_2Cl_2 used as eluents. Complex **4** was obtained as a bright red solid in 44% yield. *Method 2.* In a glove box, $PBnPh_2$ (0.032 g, 0.12 mmol) was weighed in a small flask. Next, $Pd(OAc)_2$ (0.0263 g, 0.116 mmol) and SiO_2 (0.0434 g; 375 mg per 1.00 mmol of the preligand; 100–230 mesh SiO_2) were added and the components were vigorously mixed using a spatula for approximately 1 min. The flask was topped with cotton and placed on a sand bath preheated to 50 °C and left to stir for 72 h. The reaction mixture was transferred into a glass filter and the crude product was washed from SiO_2 using acetone (5×10 mL). Then LiCl (0.0196 g, 0.462 mmol) was added and the mixture was stirred overnight. After solvent removal on a rotavapor, the crude product was dissolved in CH_2Cl_2 (30 mL) and the solution formed was filtered. Crystallization from a CH_2Cl_2 solution at rt afforded X-ray suitable red crystals of complex **4** in 90% yield (23.4 mg). R_f 0.45 (CH_2Cl_2); m.p. 230–233 °C (decomp.; lit. data [9,47]: 242–243 °C); ^{1}H NMR: 3.83 (d, 2H, $^2J_{HH} = 13.0$, CH_2), 6.83 (d, 2H, $^3J_{HH} = 7.2$, *o*-H of PBn), 7.02 (m, 2H, *m*-H of PBn), 7.11 (m, 1H, *p*-H of PBn), 7.30 (m, 4H, *m*-H of PPh), 7.44 (m, 2H, *p*-H of Ph), 7.50 (m, 4H, *o*-H of PPh); $^{31}P\{^1H\}$ NMR: 17.11 (lit. data [9,47]: 31.79 and 31.71 ppm, $CDCl_3$-d_6-DMSO relative to 85% H_3PO_4); $^{13}C\{^1H\}$ data were not obtained due to a poor solubility of the complex. Anal. Calcd for $C_{38}H_{34}Cl_4P_2Pd_2$: C, 50.31; H, 3.78%. Found: C, 49.82; H, 3.69%.

Dichlorotris(benzyldiphenylphosphine)palladium(II) (**5**). For the procedure, see the Experimental Section for complex **1**. R_f 0.14 (CH_2Cl_2); m.p. 135–137 °C (decomp.). ^{1}H NMR: 3.65 (d, 2H, $^2J_{HH} = 14$, CH_2), 7.09 (m, 2H, *o*-H of PBn), 7.17 (m, 3H, *m*- and *p*-H of PBn), 7.44 (m, 4H, *m*-H of PPh), 7.50 (m, 2H, *p*-H of Ph), 7.69 (m, 4H, *o*-H of PPh); $^{31}P\{^1H\}$ NMR: 15.06 (br. s); $^{13}C\{^1H\}$ NMR: 38.3 (d, $^1J_{CP} = 67$, CH_2), 127.3 (d, $^4J_{CP} = 2.5$, *m*-C of PBn), 128.8 (d, $^5J_{CP} = 2.3$, *p*-C of PBn), 129.0 (d, $^3J_{CP} = 12$, *o*-C of PBn), 130.6 (d, $^3J_{CP} = 5$, *m*-C of PPh), 131.4 (d, $^2J_{CP} = 8$, *ipso*-C of PBn), 131.6 (d, $^2J_{CP} = 10$, *o*-C of PPh), 132.2 (br. d, $^1J_{CP} = 99$, *ipso*-C of PPh), 132.3 (d, $^4J_{CP} = 2.5$, *p*-C of PPh). Anal. Calcd for $C_{57}H_{51}Cl_2P_3Pd$: C, 68.03; H, 5.11%. Found: C, 67.65; H, 5.42%.

Crystallographic data for complexes 1, *cis*-3, *trans*-4 and $BnPh_2P=O$ have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications Nos. CCDC-814667, 814666, 814664 and 814665, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.2. X-ray procedure

Suitable single crystals were coated with Paratone N oil, affixed to Mitegen or Litholoop crystal holders and centered on the diffractometer in a stream of cold nitrogen. Reflection intensities were collected with a Bruker Apex diffractometer, equipped with an Oxford Cryosystems 700 Series Cryostream cooler, operating at 173 K. Data were measured with ω scans of 0.3° per frame for 20 s until a complete hemisphere of data had been collected. Cell parameters were retrieved using SMART software and reduced with *SAINT-plus*, which corrects for Lorentz and polarization effects and crystal decay. Empirical absorption corrections were applied with *SADABS*. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with *SHELXL-97* incorporated into in *SHELXTL*, version 6.14.

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