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Pd(II) bromide complexes of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane. Crystal structures of $[PdBr_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$, $[PdBr_{1.133}Cl_{0.867}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ and $[PdBrCl_{0.541}Me_{0.459}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CHCl_3$

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Abstract

The revised synthesis of $[PdBr_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**1**) is described. The pure complex **1** was obtained by several days reaction of $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ with an excess of KBr. Refluxing of 2 h produced partially brominated product $[PdBr_{1.133}Cl_{0.867}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**2**), thus showing that the earlier reported reaction time of 1 h is too short. The reaction of Mg and an excess of MeBr with $[PdClMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ yielded a mixture of novel complexes $[PdBrCl(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ and $[PdBrMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$. The structures were confirmed by NMR and X-ray crystallographic studies. The structures of $\mathbf{1}\cdot CH_2Cl_2$ and $\mathbf{2}\cdot CH_2Cl_2$ are isostructural, and they are also isostructural with the earlier published structure of $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$. Thus, most probably, these complexes form a solid solution where the composition of the lattice varies from dibromide complex to dichloride complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *o*-Carboranes; Palladium(II); Bromination; Solid solution; Crystal structures

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1. Introduction

Solid solutions are common in crystalline materials. A solid solution is basically a crystalline phase that can have a variable composition. Often, certain properties of materials are modified by changing the composition of the crystalline material, thus generating a solid solution. Two types of solid solution exist: interstitial and substitutional. In the case of a substitutional solid solution, the end-member phases need to be isostructural. It is sometimes difficult to directly prove that a solid solution is obtained, as good crystals are not always obtained. In this case indirect ways are needed. For instance, propylparaben and ethylparaben were found to form an almost ideal solid solution near the melting point but no adequate crystals were grown. In this case, the isostructurality of the individual components supported the solid solution [1]. There are known families of compounds, such as steroids, which tend to be isostructural. Thus, there are steroid couples that form solid solutions which are isostructural with the respective individual components [2]. We are not aware that solid solutions have ever been reported with carborane compounds.

In this work we revise the synthesis of $[PdBr_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**1**) and report the crystal structures of $\mathbf{1}\cdot CH_2Cl_2$ and $[PdBr_{1.133}Cl_{0.867}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ ($\mathbf{2}\cdot CH_2Cl_2$). The synthesis and the crystal structure of the mixture of $[PdBrCl(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**3a**) and $[PdBrMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**3b**) are included and discussed.

2. Results

2.1. Bromide and bromide–chloride substituted Pd complexes

We have reported earlier the syntheses of $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**4**) [3] and $[PdClMe(1,2\text{-}(PPh_2)_2\text{-}$

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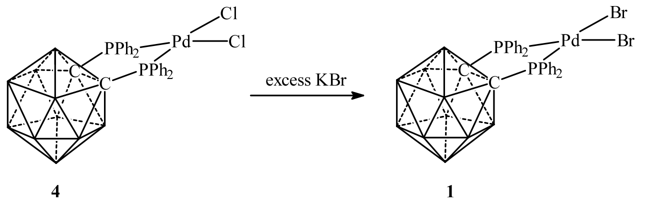
$1,2\text{-}C_2B_{10}H_{10})]$ (**5**) [4]. One methyl group has been introduced in the Pd co-ordination sphere, but we failed in introducing two. We assumed that the problem was associated to the relatively small size of chloride, and that a better leaving group such as bromide would lead to the desired $[PdMe_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$. In this aim, we planned to synthesise $[PdBr_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**1**). The procedure reported in 1986 was based on the reaction of **4** with solid KBr: the reaction mixture was heated for 1 h and the product was precipitated out with ethanol [5]. We followed the procedure using reaction time of 2 h and avoided the use of ethanol in the separation step to prevent partial degradation of the cage [6]. The ^{31}P-NMR characterisation of the isolated solid indicated, however, that a mixture of complexes was obtained. The ^{31}P-NMR of **1** should have displayed only one resonance but there were several peaks present.

Reaction time was extended for 24 h and a large excess of KBr was added. Again, only the partially brominated complex was obtained according to ^{31}P-NMR. Further reaction for 8 extra days and even a larger excess of KBr led, eventually, to the fully dibrominated complex **1**. The correct nature of **1** was unambiguously proven by chemical analysis, NMR spectra, and single crystal X-ray study. As expected, the ^{31}P-NMR in CD_2Cl_2 presented only one resonance at 77.5 ppm. The $^{11}B\{^1H\}$-NMR at 96.29 MHz displays only three resonances at δ -2.54 (2B), -3.07 (2B), and -10.29 (6B). Good crystals that permitted to define the molecular structure were grown from CH_2Cl_2–*n*-heptane. The reaction is shown in Scheme 1.

X-ray analysis of $\mathbf{1}\cdot CH_2Cl_2$ confirmed that the structure is isostructural with the earlier published structure of $\mathbf{4}\cdot CH_2Cl_2$. Both complexes crystallise in triclinic space group $P\bar{1}$ (no. 2) with $Z = 2$. Corresponding axes and angles are equal within 0.2 Å and 2°. The volumes deviate slightly, that of **1** being logically larger (21.1 Å^3) because of the bigger size of the bromide ion compared with chloride ion.

The carborane cage in $\mathbf{1}\cdot CH_2Cl_2$ is co-ordinated bidentately through P atoms to Pd(II) ion. Two bromide ions at *cis* positions complete the slightly distorted square-planar co-ordination around the metal. A perspective view of the complex unit of $\mathbf{1}\cdot CH_2Cl_2$ is given in Fig. 1, and selected bond lengths and angles are listed in Table 1.



Scheme 1. Bromination of **4**.

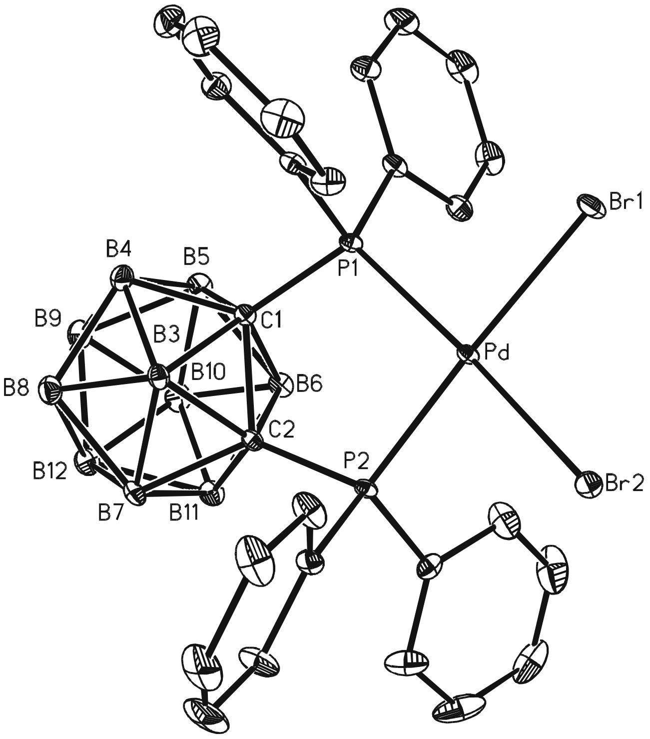


Fig. 1. Perspective view of complex unit of $\mathbf{1}\cdot CH_2Cl_2$.

Table 1
Selected bond lengths (Å) and angles (°) for complexes $\mathbf{1}\cdot CH_2Cl_2$ and $\mathbf{2}\cdot CH_2Cl_2$

	$\mathbf{1}\cdot CH_2Cl_2$	$\mathbf{2}\cdot CH_2Cl_2$
Bond lengths		
Pd–Br1	2.4745(4)	2.469(4)
Pd–Br2	2.4666(4)	2.467(3)
Pd–P1	2.2347(7)	2.234(2)
Pd–P2	2.2380(7)	2.238(2)
P1–C1	1.879(3)	1.878(8)
P2–C2	1.878(3)	1.876(8)
C1–C2	1.680(4)	1.687(11)
Bond angles		
P1–Pd–P2	92.27(3)	92.34(9)
Br1–Pd–Br2	93.879(13)	93.4(5)
P1–Pd–Br1	86.51(2)	86.8(4)
P2–Pd–Br2	88.25(2)	88.2(3)

The co-ordination sphere of $\mathbf{1}\cdot CH_2Cl_2$ is ca. planar with the co-ordinated atoms deviating not more than ± 0.16 Å from the mean co-ordination plane, and palladium deviating only 0.0263(3) Å from the plane. Planes through the atom groups Pd, P1, P2 and P1, C1, C2, P2 are close to parallel with the dihedral angle of 6.36(6)°. The Pd–P distances are close to equal as well as the Pd–Br distances. The Pd–P distances agree well with the distances found in $\mathbf{4}\cdot CH_2Cl_2$ and the Pd–Br distances with those found in $[PdBr_2(1,2\text{-}(PPh_2)_2Ph)]$ [2.4607(10) and 2.4734(10) Å] [7].

Once the ^{31}P- and ^{11}B-NMR data of **1** were well determined, we revised the earlier measured data of partially brominated products obtained with shorter reaction times. The NMR data from the products obtained at different reaction times and varying ratios of KBr were compared with the chemical shifts of **1** and **4**. We reached the conclusion that the substitution process was very gradual and that the species **4**, [PdClBr(1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$)] and **1** were present in the solution in variable amounts depending on the reaction time. Attempts to separate [PdClBr(1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$)] species to get the NMR data were unsuccessful, leading to the conclusion that the three complexes presented very similar properties resulting in difficulties in separation, and that they were all present in the same crystal. An array of beakers were set containing samples that had been produced at different reaction times and different ratios of KBr, in the aim to obtain crystals that could disclose the paradigm. Fortunately, crystals (**2**·CH_2Cl_2) were grown in one of them (reaction time 2 h) permitting to gather X-ray diffraction data.

The X-ray analysis confirmed that in **2**·CH_2Cl_2, the halide positions of the complex unit are disordered and the structure is isostructural with **1**·CH_2Cl_2 and **4**·CH_2Cl_2. Disordered halide positions have also been reported for tetra-*n*-butylammonium bromochloro[2-(1-(phenylhydrazono)ethyl)phenyl]palladate(II) [8] and [1,2-bis(phenylsulfanyl)ethane]dihalogenoplatinum(II) (dihalogeno = ClBr, ClI and BrI) [9]. In **2**·CH_2Cl_2, the halide position *trans* to P2 is occupied by 51.4(7)% bromide and 48.6(7)% chloride, and the halide position *trans* to P1 is occupied by 61.9(7)% bromide and 38.1(7)% chloride. From these values it is not possible to conclude precisely about the degree of bromination. We can assume, however, that these three complexes can be present in the crystals in variable amounts and form a solid solution. A perspective view of the complex unit of **2**·CH_2Cl_2 is given in Fig. 2 and selected bond lengths and angles are listed in Table 1. The co-ordination sphere of **2**·CH_2Cl_2 is close to planar, as expected, and the Pd–Br distances [2.467(3) and 2.469(4) Å] as well as the Pd–P distances [2.238(2) and 2.234(2) Å] are equal within experimental errors.

Comparison of the three isostructural structures **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **4**·CH_2Cl_2 reveals the expected similarity of the complex units. The Pd–Br distances in **1**·CH_2Cl_2 agree very well with the distances in **2**·CH_2Cl_2. Due to the co-ordination, the C1–C2 distance shortens from 1.722(4) Å in the free ligand [10] to 1.680(4)–1.695(5) Å in **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **4**·CH_2Cl_2. The P1–Pd–P2 angles are close to equal in all three complexes. The halogen–Pd–halogen angles in **1**·CH_2Cl_2 [93.879(13)°] and **4**·CH_2Cl_2 [93.82(5)°], and the Br1–Pd–Br2 angle in **2**·CH_2Cl_2 [93.4(5)°] are equal within experimental errors. The torsion angle P1–C1–C2–P2 is close to zero in the three isostructural complexes [0.2(2)–0.8(7)°], and thus is noticeably smaller than in the free ligand [−10.9(3)°].

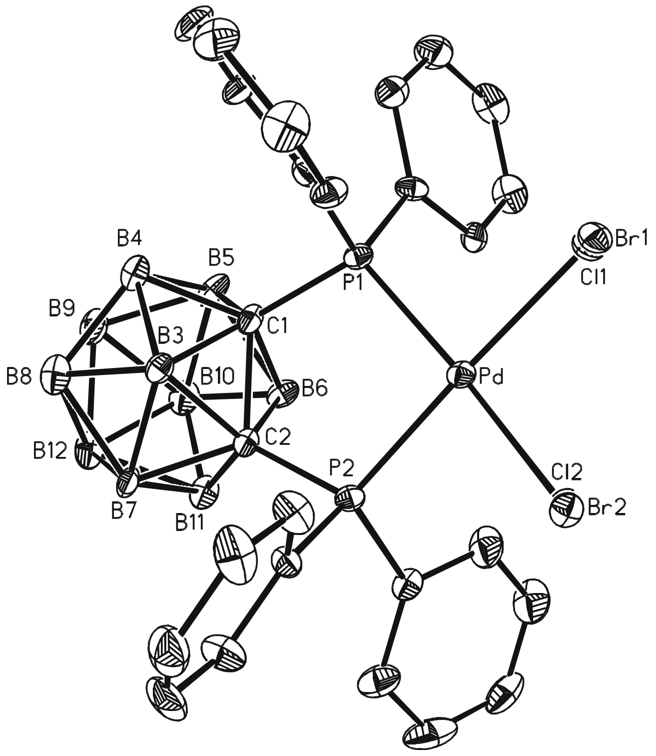


Fig. 2. Perspective view of complex unit of **2**·CH_2Cl_2.

2.2. *Bromide–methyl and bromide–chloride substituted Pd complexes*

In order to get the pure bromide–chloride substituted palladium complex, instead of the above obtained disordered complex **2**. CH_2Cl_2, [PdClMe(1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$)] (**5**) was mixed with an excess of MeBr, which has been used as a brominating agent for Pd(II) complexes [11]. No reaction, however, took place, which was confirmed by NMR spectra. In a further experiment a freshly prepared mixture of magnesium with an excess of MeBr was allowed to react with **5** for 24 h. The ^{31}P{^{1}H}-NMR spectrum indicated the existence of two asymmetric complexes in the solution: one complex had doublets at 60 and 80 ppm and the other had doublets at 62 and 76 ppm. The two species display very similar chemical shifts but it is known that replacing one chloride for bromide in Pd(II) complexes does not alter much the chemical shifts of ^{31}P{^{1}H}-NMR spectrum [12]. Crystals of complex **3** were obtained from a $CHCl_3$ solution of the product mixture layered with *n*-hexane.

Single crystal X-ray study of **3**·$CHCl_3$ confirmed that the complex unit is partially disordered consisting of the mixture of two complexes: [PdBrCl(1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$)] (**3a**, 54.1(13)%) and [PdBrMe(1,2-$(PPh_2)_2$-

$1,2\text{-}C_2B_{10}H_{10})]$ (**3b**, 45.9(13)%). Co-ordinating behaviour of the common ‘$Pd(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})$’ moiety of **3**·$CHCl_3$ is similar to the complexes **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **4**·CH_2Cl_2. In the slightly distorted square-planar co-ordination sphere of **3**·$CHCl_3$, Br occupies one position while the other ancillary ligand position is disordered with Cl and Me. A perspective view of the complex unit of **3**·$CHCl_3$ is given in Fig. 3, and selected bond lengths and angles are listed in Table 2. The synthesis of the mixture of **3a** and **3b** is shown in the Scheme 2. The structure of **3**·$CHCl_3$ is not isostructural with the structures of **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **4**·CH_2Cl_2 because of the different crystal systems and the solvents (see Table 3).

One striking feature in the structure of **3**·$CHCl_3$ is the marked difference in Pd–P distances. As a consequence of the different *trans* influence of the Me group and Br ion, the Pd–P2 bond *trans* to Me is clearly longer [2.3332(17) Å] than the Pd–P1 bond [2.2354(16) Å] *trans* to Br, and, as a consequence, the P1–Pd–P2 angle is smaller in **3**·$CHCl_3$ [88.52(6)°] than in **1**·CH_2Cl_2 [92.27(3)°] and **2**·CH_2Cl_2 [92.34(9)°]. *Trans* influence like this was noticed earlier in **5**, too [4]. Another marked difference between **3**·$CHCl_3$ and the three isostructural complexes is in the conformation of the molecules. In **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **4**·CH_2Cl_2 the dihedral angles between the planes through atom groups P1, Pd, P2 and P1, C1, C2, P2 are 6.36(6)–6.72(10)° while that in **3**·$CHCl_3$ is 32.38(13)°. The large dihedral angle of 25.25(11)° has also been found in methyl co-ordinated complex **5**.

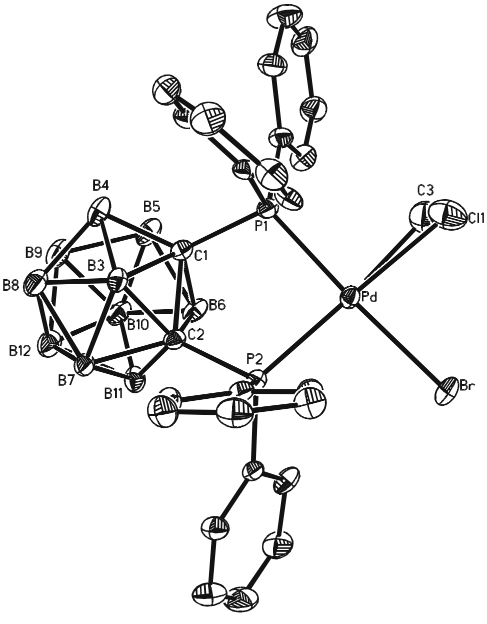
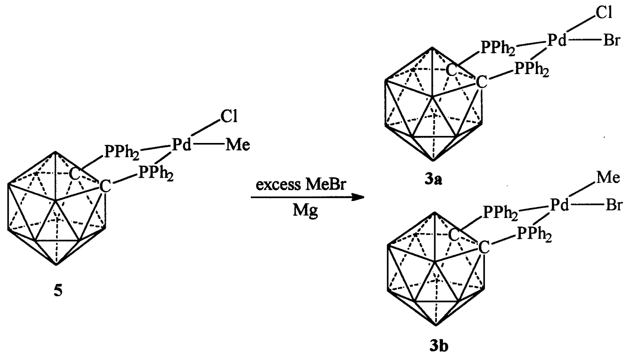


Fig. 3. Perspective view of complex unit of **3**·$CHCl_3$.

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**·$CHCl_3$

Bond lengths	
Pd–Br	2.5064(10)
Pd–Cl1	2.384(6)
Pd–P1	2.2354(16)
Pd–P2	2.3332(17)
P1–C1	1.878(6)
P2–C2	1.866(6)
C1–C2	1.698(8)
Bond angles	
P1–Pd–P2	88.52(6)
Br–Pd–Cl1	83.76(15)
P1–Pd–Cl1	92.93(16)
P2–Pd–Br	95.24(4)



Scheme 2. Partial bromination of **5**.

3. Conclusion

Solid solutions have been obtained using the *o*-carboranyldiphosphine palladium moiety ‘$Pd(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})$’, Cl and Br as ancillary ligands and CH_2Cl_2 as a solvent. The solid solutions have been formed due to the isostructurality of the end phases. This may imply that the ‘$Pd(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})$’ fragment and the solvent are very influential in defining the space group and the cell dimensions. Although there have been reported examples of substitutional solid solutions with organic compounds, examples with co-ordination compounds are deficiently described and this may represent one of the few examples where substitutional solid solutions with co-ordination compounds are found.

4. Experimental

4.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer with Universal ATR top-plate. ^1H-NMR (300.13 MHz),

Table 3
Crystallographic data for complexes **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **3**·$CHCl_3$

Complex	**1**·CH_2Cl_2	**2**·CH_2Cl_2	**3**·$CHCl_3$
Empirical formula	$C_{27}H_{32}B_{10}Br_2Cl_2P_2Pd$	$C_{27}H_{32}B_{10}Br_{1.133}Cl_{2.867}P_2Pd$	$C_{27.459}H_{32.377}B_{10}BrCl_{3.541}P_2Pd$
Formula weight	863.69	825.14	844.30
Wavelength (Å)	1.5418	0.7107	0.7107
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
Unit cell dimensions			
a (Å)	12.3310(7)	12.300(3)	13.923(3)
b (Å)	13.7086(8)	13.740(2)	16.876(3)
c (Å)	11.2000(8)	11.127(3)	15.044(3)
α (°)	109.702(5)	110.06(2)	90
β (°)	101.490(5)	100.72(2)	92.98(3)
γ (°)	85.342(5)	85.57(2)	90
V (Å^3)	1746.50(19)	1735.4(7)	3530.0(12)
Z	2	2	4
D_{calc} (g cm^{-3})	1.642	1.579	1.589
μ (cm^{-1})	93.79	21.72	20.38
$R_1(F_o)$ [a] $[I > 2\sigma(I)]$	0.0302	0.0590	0.0575
$wR_2(F_o^2)$ [b] $[I > 2\sigma(I)]$	0.0778	0.1260	0.1249

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

$^{13}C\{^1H\}$-NMR (75.47 MHz), $^{31}P\{^1H\}$-NMR (121.48 MHz) and ^{11}B-NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B-NMR spectra were referenced to external $BF_3 \cdot OEt_2$ and those for ^1H- and $^{13}C\{^1H\}$-NMR spectra were referenced to $SiMe_4$. Chemical shift values for $^{31}P\{^1H\}$-NMR spectra were referenced to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million downfield from Me_4Si, and all coupling constants are reported in Hz.

4.2. Materials

Unless otherwise noted, all manipulations were carried out under an argon atmosphere using standard vacuum line techniques. Diethyl ether was distilled from sodium benzophenone before use. Dichloromethane was dried over molecular sieves and deoxygenated prior to use. All other solvents were of reagent grade quality and used without further purification. Compound **4** [3] and **5** [4] were synthesised by published methods.

*4.3. Synthesis of **1***

A mixture of **4** (0.050 g, 0.072 mmol) and KBr (0.090 g, 0.72 mmol) in CH_2Cl_2 (8 ml) was refluxed for 24 h. After cooling, water (10 ml) was added and the organics were extracted with CH_2Cl_2 (3 × 5 ml). Combined organics were dried over Na_2SO_4. Yellow filtrate was concentrated and layered with *n*-hexane. As obtained precipitate was not dibrominated complex, the reaction was continued. Precipitate and decanted solvent were combined and dried in vacuo. KBr (0.43 g, 3.6 mmol) and CH_2Cl_2 (10 ml) were added and the solution was refluxed for 8 days. Work up was done as above. Solution was decanted and the precipitate was dried in vacuo (0.05 g, 83%). Anal. Calc. for $C_{26}H_{10}B_{10}Br_2P_2Pd \cdot CH_2Cl_2$: C, 37.54; H, 3.73. Found: C, 37.35; H, 3.73%. IR: ν [cm^{-1}] = 3060, 2963 (C_{aryl}–H), 2595, 2571, 2558 (B–H), 1437, 1091, 999, 748, 728, 685 (phosphines). ^1H-NMR (CD_2Cl_2, 25 °C): $\delta = 8.34$–8.28 (m, H_{aryl}, 5H), 7.77–7.72 (m, H_{aryl}, 5H), 7.67–7.63 (m, H_{aryl}, 10H), 3.60–1.00 (10H, B–H). $^1H\{^{11}B\}$-NMR (CD_2Cl_2, 25 °C): $\delta = 8.34$–8.28 (m, H_{aryl}, 5H), 7.77–7.72 (m, H_{aryl}, 5H), 7.67–7.63(m, H_{aryl}, 10H), 2.59 (br s, B–H, 2H), 2.47 (br s, B–H, 3H), 2.22 (br s, B–H, 2H), 2.12 (br s, B–H, 3H). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 25 °C): $\delta =$ 136.28 (s, *o*-C_{aryl}), 133.58 (s, *p*-C_{aryl}), 128.58 (s, *m*-C_{aryl}), 126.55 (s, *ipso*-C_{aryl}), 125.78 (s, *ipso*-C_{aryl}), 88.14 (dd, ^1J(C, P) = 12.48 and 13.87 = 13.78, C_c). ^{11}B-NMR (CD_2Cl_2, 25 °C): $\delta = -2.54$ (d, ^1J(B, H) = 101.10, 2B), -3.07 (d, ^1J(B, H) = 140.62, 2B), -10.29 (6B). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 25 °C): $\delta = 77.5$.

*4.4. Synthesis of **2***

A mixture of **4** (0.10 g, 0.14 mmol) and KBr (0.070 g, 0.56 mmol) in CH_2Cl_2 (2 ml) was refluxed for 2 h. After cooling, water (10 ml) was added and the organics were extracted with CH_2Cl_2 (3 × 5 ml). Combined organics were dried over Na_2SO_4. Yellow filtrate was concentrated and layered with *n*-hexane. Solution was decanted and the precipitate was dried in vacuo (0.12 g). Crystals for X-ray analysis were grown from CH_2Cl_2–*n*-hexane. IR: ν [cm^{-1}] = 3053 (C_{aryl}–H), 2593, 2557 (B–

H), 1437, 1092, 1000, 752, 730, 687 (phosphines). ^{11}B-NMR (C D_2Cl_2, 25 °C): $\delta = -2.31$ (d), -3.39 (d), -10.48. ^{31}P{^{1}H}-NMR (CD_2Cl_2, 25 °C): $\delta = 78.8$ (s, **4**); 78.4 (d, ^2J(P, P) = 14.4, **2**), 76.5 (d, ^2J(P, P) = 14.4, **2**); 76.5 (s, **1**).

*4.5. Synthesis of the mixture of **3a** and **3b***

Bromomethane (0.70 ml, 1.4 mmol, 2 M solution in Et_2O) was added slowly to a mixture of magnesium chips (0.004 g, 0.15 mmol) and one iodine crystal in Et_2O (3 ml). A reaction mixture was warmed slightly at the beginning of addition of bromomethane. The mixture was stirred at ambient temperature until most of the magnesium was dissolved.

Freshly prepared bromomethane–magnesium solution was added slowly to a Et_2O (5 ml) suspension of **5** (0.095 g, 0.14 mmol) in a cold bath (ca. −80 °C). The mixture was stirred at the cold bath for 3.5 h, and allowed to warm up to ambient temperature overnight. The mixture was stirred until total reaction time was 24 h. The crude product was obtained after filtration and dissolved in $CHCl_3$. A solution was concentrated and layered with *n*-hexane. Orange precipitate of **3** was obtained, the solvent was removed, and the product was dried in vacuo. More product was obtained from the concentrated solvent after layering with *n*-hexane (0.06 g, 60%). Anal. Calc. for $C_{26.459}H_{31.377}B_{10}Cl_{0.541}P_2Pd$: C, 43.84; H, 4.36. Found: C, 43.01; H, 4.48%. IR: ν [cm^{-1}] = 3060, 2960 (C_{aryl}–H), 2624, 2588 (B–H), 1437, 1241, 1094, 755, 504 (phosphines). ^{1}H-NMR ($CDCl_3$, 25 °C): $\delta = 0.85$ (dd, $^3J(P, H)_{trans} = 7.83$, $^3J(P, H)_{cis} = 4.8$, CH_3, 3H); 1.27–3.1 (br, B–H, 10H); 7.53–7.63 (m, H_{aryl}, 12H), 8.09–8.26 (m, H_{aryl}, 8H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 25 °C): $\delta = 129.35$ (*m*-C_{aryl}); 132.82 (*p*-C_{aryl}), 133.56 (*p*-C_{aryl}); 136.52 (*o*-C_{aryl}). ^{11}B-NMR ($CDCl_3$, 25 °C): $\delta = -0.63$ (d), -2.85 (d), -9.06. ^{31}P{^{1}H}-NMR ($CDCl_3$, 25 °C): $\delta = 60.0$ (d, ^2J(P, P) = 40.0), 79.7 (d, ^2J(P, P) = 40.0); 61.7 (d, ^2J(P, P) = 40.0), 76.1 (d, ^2J(P, P) = 40.0).

4.6. X-ray crystallographic study

Orange crystals of **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **3**·$CHCl_3$ were grown from CH_2Cl_2–*n*-heptane, CH_2Cl_2–*n*-hexane and $CHCl_3$–*n*-hexane, respectively. Single-crystal data collection was performed at −80 °C on CAD-4 diffractometer using graphite monochromatized Cu–K_α radiation for **1**·CH_2Cl_2, and on a Rigaku AFC7S diffractometer using graphite monochromatized Mo–K_α radiation for **2**·CH_2Cl_2 and **3**·$CHCl_3$. The data obtained were corrected for Lp effects. Corrections for empirical absorption (ψ scan) were also applied. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 techniques using the SHELX-97 program package [13]. The solvent of **1**·CH_2Cl_2 is disordered assuming two neighbouring positions. Partially occupied carbon atoms (C37a and C37b) of the solvent were refined with isotropic but the rest of non-hydrogen atoms with anisotropic displacement parameters. For **2**·CH_2Cl_2, refinement of the non-hydrogen atoms confirmed that both halogen positions were partially occupied by bromine and chlorine. For getting reasonable bond parameters for the chlorine atoms, DFIX restraint 2.34(1) Å was utilised for the Pd–Cl distances and equivalent displacement parameters were used for the partially occupied neighbouring chlorine and bromine atoms. As for **1**·CH_2Cl_2, the solvent of **2**·CH_2Cl_2 is disordered assuming two neighbouring positions. The partially occupied carbon atoms (C37a and C37b) of the solvent were refined with isotropic but the rest of non-hydrogen atoms with anisotropic displacement parameters. For **3**·$CHCl_3$, refinement of the non-hydrogen atoms confirmed that the bromine position is fully occupied but the other ancillary ligand position is partially occupied by chlorine atom [site occupation factor 0.541(13)] and methyl group [site occupation factor 0.459(13)]. In the refinement, DFIX restraint of 2.12(1)Å were used for the Pd–C3 distance. The partially occupied methyl carbon C3 was refined with isotropic but the rest of non-hydrogen atoms with anisotropic displacement parameters. For **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **3**·$CHCl_3$ hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters. Crystallographic data are listed in Table 3.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 171371, 171370 and 171369 for **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **3**·$CHCl_3$, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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