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Study of the *o*-carboranyl fragment as an uncommon substituent. Crystal structures of $[PdClMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ and $[PdClMe(1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$

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Abstract

The syntheses of two novel *o*-carboranyl palladium complexes $[PdClMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ and $[PdClMe(1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ are described and their crystal structures are determined. Both complexes were obtained in CH_2Cl_2 by two methods: (i) by replacement of 1,5-cyclooctadiene (cod) in [PdClMe(cod)] by $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and $1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and (ii) by the reaction of $[PdCl_2(1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (R = Ph, ^{i}Pr) with $SnMe_4$. In both complexes the carborane cage is co-ordinated bidentately through P atoms to the Pd(II) ion, while the Cl ion and Me group in *cis* positions complete the distorted square-planar co-ordination around the metal. Differences in the ^{31}P-NMR spectra of $PdCl_2$ complexes of *o*-carboranyl diphosphines and of organic diphosphines with ethane and benzene backbones are discussed. The ^{31}P-NMR spectra of *o*-carboranyl $PdCl_2$ complexes have been compared with spectra of other complexes having same metal surrounding. The data obtained allowed an interpretation of the electronic characteristics of *o*-carborane and of the influence of these on co-ordination capacity.

Keywords: *o*-Carboranes; Palladium(II); ^{31}P-NMR; Diphosphine; Crystal structures

1. Introduction

The *o*-carborane $1,2\text{-}C_2B_{10}H_{12}$ is an icosahedral cluster with the two carbon atoms in adjacent positions. One way to comprehend the orbital set of *o*-carborane is to consider that each participating atom contributes with two sp and two p_t (tangential orbital on cluster carbon) orbitals. This situation is very similar to the atomic orbitals participating in the molecular orbitals of acetylene. In the same way, then, the hydrogen atom connected to the cage carbon (C_c) in *o*-carborane is acidic and may be removed by strong bases. Moreover, the *o*-carborane cluster is extremely electron withdrawing for the C_c substituents. During our research [1–5], we have observed many structural features, as well as reactivity behaviour that makes the *o*-carboranyl fragment unique in organic chemistry.

Bidentate ligands have played an important role in the development of catalytic applications of metal organic complexes since 1959 [6]. The steric properties of diphosphines are determined by the four substituents at the two phosphorus atoms and the length of the spacer. In general, the most stable complexes are obtained when a five-membered chelate ring is formed with the metal, i.e. when the bridge between the two phosphorus donor atoms consists of two carbon atoms. This occurs for octahedral and square–planar complexes in which the preferred P–M–P bite angle is about 90° [6a].

In an effort to define the unique properties of the *o*-carborane cluster, we initiated a search for probes that, as quantitatively as possible, could demonstrate these properties. In this work, we focus our attention on *closo* *o*-carboranyldiphosphines and their co-ordinating capability towards Pd(II), and analyse the differences in the ^{31}P-NMR spectra of the ligands and their

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complexes. To reveal the influence of spacer in the diphosphine ligand, comparison is made with the ^{31}P-NMR spectra of corresponding diphosphines with ethane and benzene as backbone and their $PdCl_2$ complexes. We also report the syntheses of [PdClMe(1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$)] (**5**) and [PdClMe(1,2-$(P^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$)] (**6**), and the crystal structures of **5**·CH_2Cl_2 and **6**.

2. Results

As we have demonstrated earlier [7], the reaction of *o*-carboranyldiphosphines with transition metal complexes in methanol or ethanol leads to deboronation of the *closo* *o*-carboranyl cluster to produce 11-vertex monoanionic *nido* species. As is clear, care needs to be taken in attempting the synthesis of transition metal complexes incorporating the 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) and 1,2-$(P^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$ (**2**) ligands (Fig. 1); for deboronation seems to be the favoured process if a nucleophile is present.

Drawing on our earlier experiences with *o*-carboranyldiphosphines [2a,7a,7b,8], we were able to synthesise the monoalkyl derivatives **5** and **6** without the use of nucleophilic solvents. Two methods, relying on CH_2Cl_2 as a solvent, were employed (see Fig. 1). Method A consists of the replacement of 1,5-cyclooctadiene (cod) in [PdClMe(cod)] by **1** or **2**, while method B consists of the replacement of one Cl ion in **3** and **4** by a Me group from $SnMe_4$. The reaction conditions were similar to the conditions used in the synthesis of [PdClMe(cod)] [9].

Complex **5** was obtained in 80% yield by both methods. The ν(B–H) resonances in the IR spectrum at 2616, 2572 and 2546 cm^{-1} are in agreement with a *closo* structure of the *o*-carboranyl fragment; the ^{11}B-NMR spectrum points to the same structure, with a 2:3:5 pattern in the range -1.12 to -9.68 ppm. While the ^{11}B-NMR spectrum does not provide any information about the average C_s symmetry of the complex, the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra confirm the expected C_s symmetry. The ^{1}H-NMR resonance for Me at $\delta = 0.68$ ppm is split by the two chelating phosphorus nuclei, with $^{3}J(P,H) = 8.10$ and 4.29 Hz, conforming the non-equivalence of the two phosphorus atoms. Unlike the ^{1}H-NMR spectrum, the $^{13}C\{^{1}H\}$-NMR spectrum does not show this non-equivalence. The Me group displays a single resonance at $\delta = 15.41$ ppm, which is split only by one of the P atoms, most probably the one *trans* to Me. This yields a doublet with $^{2}J(P,C) = 101.3$ Hz. The $^{31}P\{^{1}H\}$-NMR spectrum is consistent with the C_s symmetry, yielding resonances at $\delta = 59.16$ and 80.54 ppm. Each resonance is split by the other phosphorus with $^{2}J(P,P) = 39.6$ Hz.

The synthesis of complex **6** by methods A and B did not proceed as for **5**. Whereas method A yielded **6** in almost the same manner and yield as it did **5**, method B provided only a 37% yield after 10 days and with considerable excess of $SnMe_4$. Characterisation of **6** by ^{1}H-, ^{13}C- and ^{31}P-NMR confirmed the similarity to **5**. The ^{1}H-NMR resonance of the Me group for **6** appears at $\delta = 0.81$ ppm, and $^{3}J(P,H)$ values of 7.50 and 3.45 Hz show that Me group is coupled unequally to the two P nuclei. Some differences between **5** and **6** are apparent, however. A major difference appears in the Pd–Me resonance in the $^{13}C\{^{1}H\}$-NMR spectrum, which for **6** is observed upfield at $\delta = 6.90$ ppm. This resonance shows coupling of the methyl to just one phosphorus atom. As for **5**, the $^{31}P\{^{1}H\}$-NMR spectrum shows two resonances at $\delta = 82.22$ and 104.43 ppm with a common $^{2}J(P,P)$ of 30.9 Hz. The ^{11}B-NMR spectrum, with

Fig. 1. Synthesis of the [PdClMe(1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$)] complexes. R is Ph for **1**, **3**, **5** and ^{i}Pr for **2**, **4**, **6**.

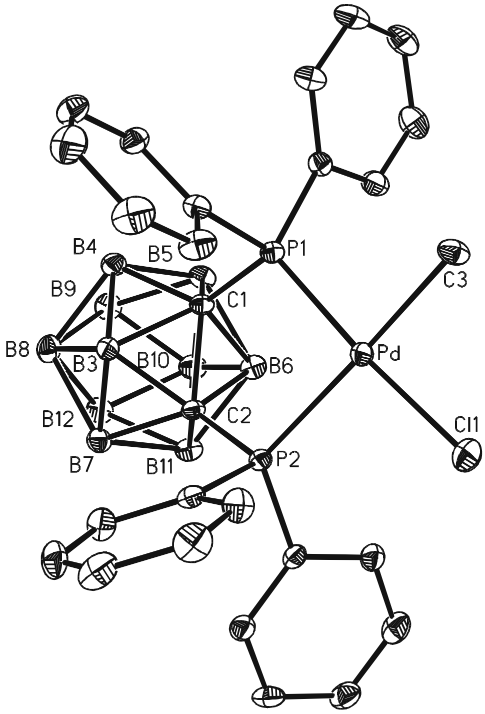

Fig. 2. Perspective view of **5**.

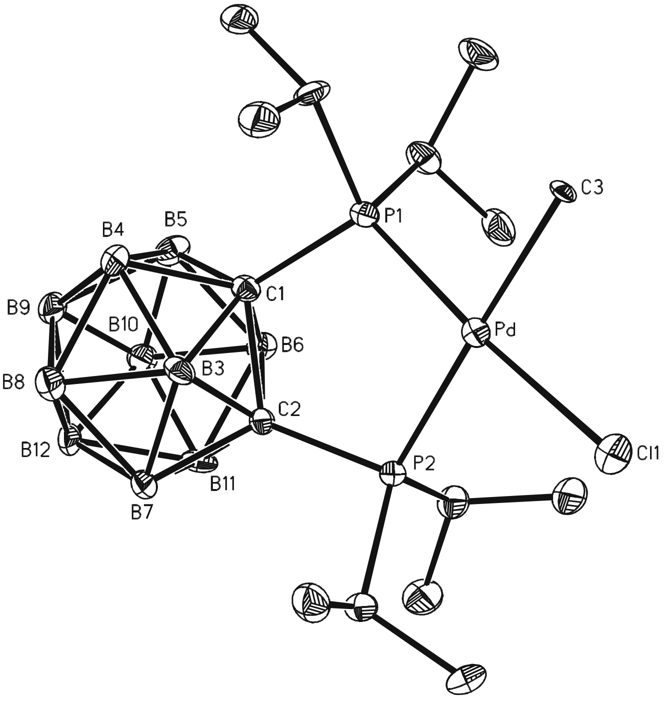

Fig. 3. Perspective view of **6**.

a 3:2:5 pattern in the range 0.02 to −10.19 ppm, provides no evidence for the C_s symmetry of the complex.

To allow unambiguous determination of the molecular structures of complexes **5** and **6**, we grew crystals from dichloromethane and dichloromethane–*n*-hexane, respectively. The common moieties of compounds **5** and **6** are very similar. In both compounds, the carborane cage is co-ordinated bidentately through P atoms to the Pd(II) ion, and the Cl ion and the Me group in *cis* positions complete the distorted square–planar co-ordination around the metal. Perspective views of the complex units are presented in Figs. 2 and 3, and selected bond lengths and angles are listed in Table 1.

The geometry of the common moieties of **5** and **6** is quite similar, too. The co-ordination spheres are ca. planar and the dihedral angles between the planes through the atom groups Pd,P1,P2 and P1,C1,C2,P2 are almost the same [25.25(11) and 22.5(3)° for **5** and **6**, respectively]. The P1–Pd–P2 bite angles are close to 90° in both complexes [90.48(5) and 91.53(7)° for **5** and **6**]. The most striking feature of the structures of **5** and **6** is the marked difference in the Pd–P distances. As a consequence of the different *trans* influence of the Me group and Cl ion, the Pd–P2 bonds, which are *trans* to Me, are clearly longer [2.3181(12) and 2.3507(19) Å, for **5** and **6**] than the Pd–P1 bonds, which are *trans* to Cl [2.2143(13) and 2.232(2)° Å, for **5** and **6**]. The Pd–P1 distances in **5** and **6** are equal or differ only slightly from the values observed for the corresponding distances in **3** and **4** [2.2284(14)–2.243(3) Å] [8,10].

3. Discussion

Pd(II) complexes with $PdCl_2$ moiety can suitably be used to probe the differences between organic diphosphines and *o*-carboranyldiphosphines because only one isomer is possible and several examples of complexes with organic diphosphines are available in the literature. Furthermore, and very usefully, diphosphines are easily studied by ^{31}P-NMR.

Table 1
Selected bond lengths (Å) and angles (°) for complexes $\mathbf{5}\cdot CH_2Cl_2$ and **6**

	$\mathbf{5}\cdot CH_2Cl_2$	**6**
Bond lengths		
Pd–Cl1	2.3454(16)	2.365(2)
Pd–C3	2.114(5)	2.157(6)
Pd–P1	2.2144(14)	2.232(2)
Pd–P2	2.3179(13)	2.3507(19)
P1–C1	1.892(5)	1.882(7)
P2–C2	1.877(5)	1.879(7)
C1–C2	1.694(6)	1.724(9)
Bond angles		
P1–Pd–P2	90.48(5)	91.53(7)
C3–Pd–Cl1	85.89(15)	86.10(18)
P1–Pd–C3	88.45(15)	88.85(18)
P2–Pd–Cl1	95.02(5)	93.50(7)

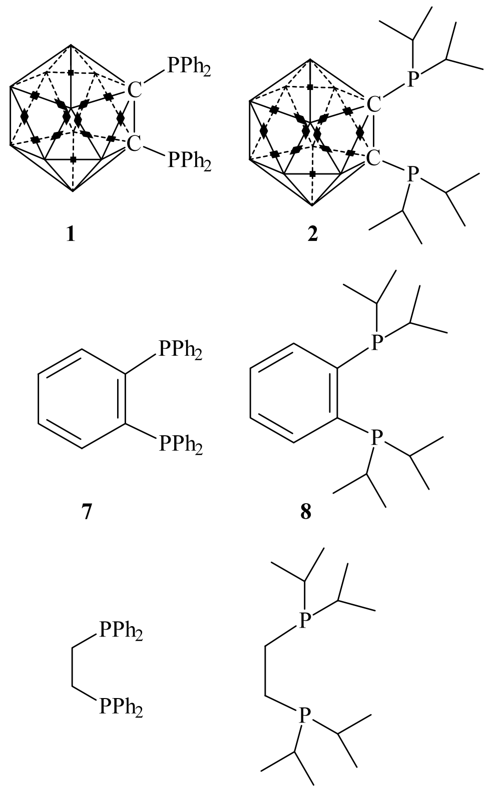

Fig. 4. Investigated (**1**, **2**) and compared (**7**–**10**) diisopropyl and diphenylphosphine ligands.

Table 2
$^{31}P\{^1H\}$-NMR chemical shift and ccs data for [$PdCl_2$(P–P)] complexes of diphosphines with electron donating (^{i}Pr) (**2**, **8**, **10**) and electron withdrawing (Ph) (**1**, **7**, **9**) groups, in ppm

Ligand	δ (Ligand)	δ (Complex)	ccs	References
2	32.8	69.1	36.3	[1d,8]
8	−5.3	92.3	97.6	[11b]
10	9.4	100.7	91.3	[11c,24]
1	7.73	78.3	70.6	[20,8]
7	−13.6	64.4	78.0	[11a,25]
9	−13.2	64.2	77.4	[11b,26]

ccs = δ (complex) − δ (ligand).

Ligands **1** and **2** were chosen because they permitted comparison with the comparable organic ligands 1,2-bis(diphenylphosphino)benzene (**7**), 1,2-bis(diisopropylphosphino)benzene (**8**), 1,2-bis(diphenylphosphino)ethane (**9**) and 1,2-bis(diisopropylphosphino)ethane (**10**), which contain benzene and ethane backbones and whose ^{31}P-NMR data are available in the literature (Fig. 4) [11]. The position of the phosphorus atoms in ligands **1** and **2**, together with the rigidity of the cluster, makes their chelating sites more similar to the chelating sites in **7** and **8** than in **9** and **10**. However, comparison of the X-ray diffraction analyses of [$PdCl_2$(**8**)] and [$PdCl_2$(**9**)] has shown that there are no major structural deviations in the neighbourhood of the metal [11b,12]. This led us to suppose that the *o*-carboranyl fragment would not introduce major structural changes, and would allow fruitful comparison of our complexes **3** and **4** with complexes where the two phosphine fragments of the chelating ligand were connected with an ethane or benzene backbone.

Low values of the dihedral angles between the planes P–C_c–C_c–P and P–Pd–P observed for **5** and **6** in solid state [25.25(11) and 22.5(3)°, respectively (see above)] suggest that the energy barrier needed to flip to the reciprocal conformer is very low. In solution these conformers could be expected to average to a complex where two C_c, two P, Pd, Cl and methyl carbon atoms lie in a plane. Thus, both **5** and **6** can be assumed to present an averaged C_s geometry in solution. This should imply a 2:2:2:2:1:1 or similar pattern in the ^{11}B-NMR spectra, which is in agreement with the spectra obtained at room temperature.

3.1. The $PdCl_2$ fragment as probe

The $PdCl_2$ fragment was chosen as to produce symmetric [$PdCl_2$(P–P)] complexes that would generate only one ^{31}P-NMR resonance. Table 2 compares two sets of data, the first for diphosphines with electron-donating groups (^{i}Pr) and the second for diphosphines with electron withdrawing groups (Ph) on P. The backbone varies in the same way in the two sets: *o*-carborane, benzene and ethane in **2**, **8** and **10**, and in **1**, **7** and **9**, respectively (see Fig. 4).

The δ values range widely, but our interest is the co-ordination chemical shift (ccs) value [ccs = δ(Complex) − δ(Ligand)] [13]. For the first set, the ccs values are comparable for **8** (benzene) and **10** (ethane), 97.6 and 91.3 ppm, respectively, but the value drops to 36.3 ppm for **2** (*o*-carborane). Although the ccs values of the second set are more similar, at 78–70 ppm, the same trends are found as for the isopropylphosphines: comparable ccs values for the benzene–ethane and a lower value for the *o*-carborane.

Can this effect of the *closo* *o*-carboranyl fragment be explained? In order to answer this question, we first look at another important difference between the *o*-carborane, benzene and ethane backbones when present in the same type of diphosphines.

The nuclear magnetic shielding, which gives rise to the chemical shift δ, is distinguished usually into diamagnetic σ^d and paramagnetic σ^p shielding terms. For ^{31}P-NMR, it is generally accepted that the σ^p term is very important in explaining the chemical shifts [14]. Since this term not only depends on the ground electronic state of the molecule but also on a sum over excited states, it is usually difficult to discuss the ^{31}P-

NMR chemical shifts qualitatively. However, additive data to calculate the ^{31}P-NMR chemical shifts for primary, secondary and tertiary phosphines [15] and a good linear correlation between the chemical shift of a tertiary phosphine and the change in the chemical shift upon co-ordination are provided in the literature [16]. The ring contribution to the ^{31}P-NMR chemical shifts of transition metal phosphorus chelate complexes has been noted [17]. We have also found that for *closo* *o*-carboranylphosphines, plausible explanations of the chemical shift can be given solely in respect of the σ^{d} term [1a,18]. This makes sense if it is considered that a strong σ^{p} term is a consequence of low-lying unoccupied orbitals ψ^* which allow efficient combination with suitable energy-rich occupied orbitals. According to selection rules, the combination of an occupied and an unoccupied orbital is magnetically active only when the corresponding (hypothetical) electron transfer comprises an angular momentum [19]. Perpendicularly placed lp/$p_{\perp}^{*}$ combinations (lp = lone pair, $p_{\perp}^{*}$ = participating atomic orbital in low-lying unoccupied molecular orbital ψ^*, perpendicular to lp) are active in NMR, yielding deshielding contributions perpendicular to the lp/ψ^* plane of charge circulation. Such deshielding is unlikely, however, as it seems that while the lp corresponds to the HOMO, the LUMO would be more centered on the cluster or the aromatic ring. In our view, then, the σ^{p} term is of small relevance in *o*-carboranyl ligands.

When we examine the above argument with a look at our two *o*-carboranyldiphosphine ligands, we find that a simple diamagnetic shielding term σ^{d} does not suffice to account for the chemical shifts. If it did, one would expect $\delta\,^{31}$P for **2** to appear at higher field than $\delta\,^{31}$P for **1**. This is not the case, however: the experimental spectrum shows 32.8 ppm for **2** and 7.73 ppm for **1** [1d,20]. Thus, the real order is the reverse of that predicted on the basis of simple σ^{d} [21]. We suggest an explanation in terms of a low-lying virtual orbital, ψ^*, possibly the LUMO. If an overlap of the lp orbital of the P atom with the p_t (tangential orbital of cluster carbon) participating in ψ^* is efficient, electron density from the P atom is transferred to the cluster. This transfer would be more efficient for electron-donating groups such as ^{i}Pr than for electron-withdrawing fragments such as Ph. And as a consequence, the P atom would be more deshielded in **2** and its ^{31}P-NMR resonance would be observed at lower field.

When the phosphine binds to a metal, the lp on the P atom is no longer available for combination with the p_t (tangential orbital of cluster carbon) of the carbon atom in unoccupied molecular orbital ψ^*, as the electrons are participating in co-ordination to metal. Co-ordination produces a strong deshielding effect when electron density is transferred to the metal: thus the ^{31}P-NMR resonance will move downfield. This move downfield should be observed upon co-ordination of all diphosphines and monophosphines, and can be calculated with the help of the ccs value. Indeed, as early as the 1970s Shaw and co-workers [17] pointed out the good linear correlation between the chemical shifts of tertiary phosphines ($\delta\,^{31}$P) and the change in the chemical shift (Δ) upon co-ordination to a metal. The relationship $\Delta = A\delta\,^{31}\mathrm{P} + B$ that they observed was capable of predicting the co-ordination shifts of phosphines for a given complex, when a sufficient number of analogues were known to calculate the constants A and B. The relationship broke down, however, for the ^{31}P chemical shifts of a number of phosphorus chelate complexes.

Comparison can be made of ligands **2**, **8** and **10** and their $PdCl_2$ complexes. For purposes of the comparison, we take the values for **10** and its $PdCl_2$ complex as a reference since no interaction occurs between the lp orbital of the P atom and the p_t orbital in the ψ^* on the backbone. The calculated reference value of ccs for **10** is 91.3 ppm. The ccs value for **8** is equal to 97.6 ppm, which is close to that of **10** and would indicate that there is little interaction between the lp orbital of the P atom and the p_t orbital of ψ^*. In contrast, ccs for **2** is 36.3 ppm, and considerably smaller than ccs for **8** or **10**. This implies a strong transfer of electron-density in the free ligand, from the lp to the p_t orbitals on ψ^*. This electron transfer would explain the electron affinity of the cluster, the C_c–C_c elongation, the comparable lower basicity of the carboranylphosphines, the low co-ordinating capability and many structural changes. The same trend is evident for the 1,2-bis(diphenylphosphine) ligands **1**, **7** and **9** (Fig. 4). Again, a close similarity is observed in the ccs values of the benzene and ethane diphosphines **7** and **9**, while a smaller ccs value is found for **1**. Here, however, the difference in ccs values between the *o*-carborane derivative and the benzene and ethane derivatives is smaller.

For any fixed ring size, the deshielding produced on the P atom is due to co-ordination. The ccs value is, then, a measure of the bonding capacity of P–P, and for a similar group of ligands, the larger the ccs value the stronger is the chelating bond. Thus, **2** is a more weakly co-ordinating ligand than **8**, and **8** is comparable to the corresponding ligand **10** with ethane backbone. This result was expected on the basis of the strong electron-withdrawing capacity of the *o*-carboranyl moiety. The ccs value provides, then, a quantitative measure of the bonding capacity.

4. Experimental

4.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded with KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H-NMR (300.13 MHz), ^{13}C{^{1}H}-NMR (75.47 MHz), ^{31}P{^{1}H}-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 ^{1}H- and ^{13}C{^{1}H}-NMR spectra were referenced to $SiMe_4$. Chemical shift values for ^{31}P{^{1}H}-NMR spectra were referenced to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million (ppm) 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. [PdClMe(cod)] was prepared according to the literature method [9]. $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ [22], $1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ [1e], $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ and $[PdCl_2(1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ [8] were synthesised by published methods.

4.3. Synthesis of **5** (method A)

A mixture of **1** (0.12 g, 0.23 mmol) and [PdClMe(cod)] (0.06 g, 0.23 mmol) in CH_2Cl_2 (12 ml) was refluxed for 20 h. The mixture was filtered through Celite and the filtrate was dried in vacuo. The obtained solid was washed with cold Et_2O and dried in vacuo (0.12 g, 80%). Anal. Calc. for $C_{27}H_{33}B_{10}ClP_2Pd$: C, 48.44; H, 4.97. Found: C, 48.60; H, 5.16%. IR: ν (cm^{-1}) = 3054, 2976, 2895 (C_{aryl}–H); 2616, 2572, 2546 (B–H); 1437, 1094, 745, 689, 504 (phosphines). ^{1}H-NMR (CD_2Cl_2, 25 °C): $\delta = 0.68$ (dd, $^3J(P,H)_{trans} = 8.10$, $^3J(P,H)_{cis} = 4.29$, CH_3, 3H); 1.50–3.35 (br, B–H, 10H); 7.51–7.63 (m, H_{aryl}, 12H); 8.08–8.21 (m, H_{aryl}, 8H). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 25 °C): $\delta = 15.41$ (d, $^2J(P,C)_{trans} = 101.3$, CH_3); 86.85 (t, $^1J(C,P) = 12.49$, C_c); 91.73 (d, $^1J(C,P) = 29.13$, C_c); 126.5 (d, $^1J(C,P) = 54.10$, *ipso*-C_{aryl}), 128.2 (d, $^1J(C,P) = 33.29$, *ipso*-C_{aryl}); 129.0 (d, $^3J(C,P) = 9.71$, *m*-C_{aryl}); 132.7 (s, *p*-C_{aryl}), 133.3 (s, *p*-C_{aryl}); 136.2 (d, $^2J(C,P) = 13.87$, *o*-C_{aryl}), 136.3 (d, $^2J(C,P) = 12.48$, *o*-C_{aryl}). ^{11}B-NMR (CD_2Cl_2, 25 °C): $\delta = -1.12$ (d, $^1J(B,H) = 175$, 2B), -3.46 (d, $^1J(B,H) = 189$, 3B), -9.68 (5B). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 25 °C): $\delta = 59.16$ (d, $^2J(P,P) = 39.6$), 80.54 (d, $^2J(P,P) = 39.6$).

4.4. Synthesis of **5** (method B)

Tetramethyltin (0.03 ml, 0.21 mmol) was added dropwise to a solution of **3** (0.11 g, 0.16 mmol) in CH_2Cl_2 (10 ml). The mixture was refluxed for 20 h and filtered through Celite, and the solvent was evaporated in vacuo. The obtained solid was washed with cold Et_2O and dried in vacuo (0.089 g, 81%). Characterisation was as for method A.

4.5. Synthesis of **6** (method A)

A mixture of **2** (0.20 g, 0.53 mmol) and [PdClMe(cod)] (0.14 g, 0.53 mmol) in CH_2Cl_2 (15 ml) was refluxed for 20 h. The mixture was filtered through Celite and the filtrate was dried in vacuo. The obtained solid was washed with cold Et_2O and dried in vacuo (0.24 g, 86%). Anal. Calc. for $C_{15}H_{41}B_{10}ClP_2Pd$: C, 33.77; H, 7.75. Found: C, 33.55; H, 7.46%. IR: ν (cm^{-1}) = 3004, 2969, 2933, 2905, 2889 (C–H); 2657, 2636, 2627, 2616, 2586 (B–H); 1460, 1385, 1369, 1139, 1072, 1036, 878, 737, 639, 503 (phosphines). ^{1}H-NMR (CD_2Cl_2, 25 °C): $\delta = 0.81$ (dd, $^3J(P,H)_{trans} = 7.50$, $^3J(P,H)_{cis} = 3.45$, CH_3, 3H); 1.47–1.73 (m, CH_3, 24H); 2.75 (m, CH, 4H). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 25 °C): $\delta = 6.90$ (d, $^2J(C,P)_{trans} = 99.88$, Pd–CH_3); 19.45, 20.02, 20.53, 21.45, 21.71, 21.82 (s, CH_3); 29.83, 30.11 (CH); 86.70, 91.24 (m, C_c). ^{11}B-NMR (CD_2Cl_2, 25 °C): $\delta = 0.02$ (3B); -3.61 (d, $^1J(B,H) = 147$, 2B); -10.19 (5B). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 25 °C): $\delta = 82.22$ (d, $^2J(P,P) = 30.9$); 104.43 (d, $^2J(P,P) = 30.9$).

4.6. Synthesis of **6** (method B)

Tetramethyltin (0.03 ml, 0.25 mmol) was added dropwise to a solution of **4** (0.11 g, 0.19 mmol) in CH_2Cl_2 (10 ml). The mixture was refluxed for 21 h and filtered through Celite, and the solvent was evaporated in vacuo. The obtained solid was washed with cold Et_2O and dried in vacuo. As NMR study showed that no reaction had occurred, the synthesis was continued with the addition of CH_2Cl_2 (40 ml) and $SnMe_4$ (0.12 ml, 1.00 mmol) to the earlier obtained 'product'. The mixture was refluxed for 10 days, filtered through Celite, dried in vacuo, washed with Et_2O, and dried in vacuo. Characterisation was as for method A (0.037 g, 37%).

4.7. X-ray crystallographic study

Crystals of $\mathbf{5}{\cdot}CH_2Cl_2$ and **6** were grown from CH_2Cl_2 and CH_2Cl_2–*n*-hexane, respectively. Single-crystal data collections were performed at -80 °C on a Rigaku AFC7S diffractometer using graphite monochromatized Mo–K_α radiation. The unit cell parameters for both compounds were determined by least-squares refinement of 25 carefully centred reflections. A total of 6341 and 4742 reflections, giving 6138 and 4411 independent reflections ($R_{int} = 0.0411$ and 0.0490) were collected by $\omega/2\theta$ scan mode for **5**·CH_2Cl_2 and **6**, respectively. Both sets of data were corrected for Lorentz and polarization effects. Corrections for empirical absorption (ψ scan) were also applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELX-97 program package [23]. Non-hydrogen atoms were refined with anisotropic displacement parameters, except for C37 of the disordered CH_2Cl_2 solvent of **5**·CH_2Cl_2 with minor occupancy (0.116(7)). 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. For **5**·CH_2Cl_2, anisotropic refinement of C3, which lies close to the disordered solvent (e.g. C3···Cl3b$^{\#}$ = 3.522 Å, # = equivalent position x, $y-1$, z), resulted in abnormal thermal parameters and a residual slightly greater than 1 e Å^{-3} in the vicinity of C3. Isotropic refinement of C3, divided between two neighbouring positions, resulted in similar residuals near the two partially occupied C3 positions. Thus, in the final refinement, C3 was refined anisotropically using soft ISOR restraint. 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 161736 for **5**·CH_2Cl_2 and CCDC 161735 for **6**. 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 or www.http://www.ccdc.cam.ac.uk).

Table 3
Crystallographic data for **5**·CH_2Cl_2 and **6**

Complex	**5**·CH_2Cl_2	**6**
Empirical formula	$C_{28}H_{35}B_{10}Cl_3P_2Pd$	$C_{15}H_{41}B_{10}ClP_2Pd$
Formula weight	754.35	533.37
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
Unit cell dimensions		
a (Å)	18.141(4)	8.062(2)
b (Å)	9.873(5)	20.750(4)
c (Å)	19.173(3)	15.357(3)
β (°)	98.52(2)	103.40(3)
V (Å^3)	3396.1(19)	2499.1(9)
Z	4	4
D_{calc} (g cm^{-3})	1.475	1.418
μ (cm^{-1})	8.98	9.80
Number of unique reflections	6138	4411
Number of parameters	410	271
Goodness-of-fit on F^2	1.019	1.041
$R_1(F_o)$ [a] [$I>2\sigma(I)$]	0.0546	0.0652
$wR_2(F_o^2)$ [b] [$I>2\sigma(I)$]	0.1282	0.1467

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

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