

Revising the $[\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]$ synthesis and comparison of its behavior with $[\text{PdCl}_2(1,2-(\text{P}^i\text{Pr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]$. Crystal structure of $[\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]$

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Abstract

Two methods for the revised synthesis of $[\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]$ are described. They differ on the reagent complex, to say 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane was mixed with $[\text{PdCl}_2(\text{cod})]$ or $[\text{PdCl}_2(\text{PhCN})]$ in non-nucleophilic solvents. The structure of $[\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]$ was determined by single-crystal X-ray study. The carborane cage is coordinated bidentately through the P atoms to the Pd(II) ion, the remaining two positions are occupied by two chloride ions which are mutually *cis*. Overall, the coordination about the metal can be described as a slightly distorted square-planar. The reaction of 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane in dichloromethane produced mostly a compound with similar formula, however some deboronation took place and $[\text{Pd}_2(\mu\text{-Cl})_2\{7,8-(\text{P}^i\text{Pr}_2)_2-7,8-\text{C}_2\text{B}_9\text{H}_{10}\}_2]$ was also produced. Larger amounts of this dinuclear complex were obtained when the *closo* species was refluxed for few minutes in a mild nucleophilic solvent. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carboranes; Palladium; Deboronation; Cluster

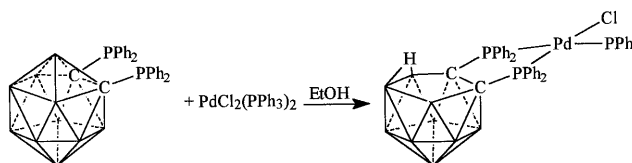
1. Introduction

Over the last 15 years enormous progress has been made in the development and design of single-site catalysts for the polymerization of α -olefins [1]. Two of the fundamentals for these catalysts are that two *cis* positions of the metal center are available to perform the reaction, and that the catalyst is cationic before insertion of the alkene. Diphosphines have already been demonstrated to be very convenient for this sort of catalysis [2]. Taking into account that *o*-carboranyldiphosphines fall into this category, and considering the importance of Pd as a metal in catalysts, we have reinvestigated the synthesis of $[\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]$ in an effort to determine its crystal structure. Also, considering the easy deboronation that has been demonstrated to occur in the cluster when

substituents on the carbon atoms contain lone pairs, strategies have been studied to preserve the *closo* nature of the cluster through the reaction.

2. Results and discussion

As we have demonstrated in a series of papers [3], the reaction of *o*-carboranyldiphosphines with transition metal complexes in methanol, or ethanol, leads to deboronation of the *closo* carboranyl cluster to produce 11 vertex monoanionic *nido* species. This is shown in Scheme 1.



Scheme 1. Deboronation of the *closo* cluster by metal coordination in nucleophilic solvents.

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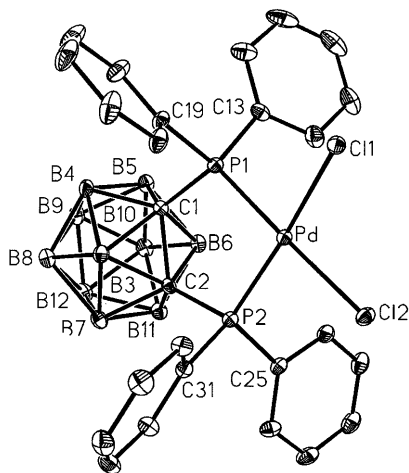


Fig. 1. Perspective view of complex unit of $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$. Thermal displacement ellipsoids are drawn at 20% probability level.

Table 1

Selected bond lengths (Å) and angles (°) for $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$

Bond lengths

Pd–P1	2.2325(13)
Pd–P2	2.2284(14)
Pd–Cl1	2.3453(14)
Pd–Cl2	2.3423(13)
P1–C1	1.876(4)
P1–C13	1.818(4)
P1–C19	1.807(4)
P2–C2	1.870(4)
P2–C25	1.809(4)
P2–C31	1.814(4)
C1–C2	1.695(5)

Bond angles

P2–Pd–P1	92.44(5)
P2–Pd–Cl2	87.24(5)
P1–Pd–Cl2	175.64(4)
P2–Pd–Cl1	173.65(4)
P1–Pd–Cl1	86.97(5)
Cl2–Pd–Cl1	93.82(5)
C2–C1–P1	113.4(3)
B4–C1–P1	125.6(3)
B5–C1–P1	124.3(3)
B3–C1–P1	115.8(3)
B6–C1–P1	114.6(3)
C1–C2–P2	114.6(2)
B7–C2–P2	125.1(3)
B11–C2–P2	124.2(3)
B3–C2–P2	115.8(3)
B6–C2–P2	115.4(3)

A nucleophilic attack by ethanol to the more positive boron atoms, either B3 or B6, takes place producing a mononegative chelating ligand. This and the chloride compensate the Pd positive charge producing a neutral Pd complex. Besides alcohols, other nucleophilic solvents may also produce the deboronation reaction.

Thus, care should be taken in attempting the synthesis of transition metal complexes incorporating the $1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ fragment, as $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$, since deboronation seems to be the favored process if a nucleophile is present. Based on the experience gained dealing with *o*-carboranyldiphosphines [3], we attempted the synthesis of $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$, avoiding the use of nucleophilic solvents. This led to a full characterization. Two methods, A and B, were used which produce a suitable and pure solid.

Following our criteria to avoid nucleophiles we have used dichloromethane and toluene. Furthermore, we even considered that nucleophilic agents had to be kept away in the separation process. This will be shown in the synthesis of $[\text{PdCl}_2(1,2\text{-(P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$. Following these restrictions the yields produced are satisfactory specially the one with $[\text{PdCl}_2(\text{cod})]$, method A, that produces $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ in 96% yield. The $\nu(\text{B-H})$ in the IR of this compound at 2580 and 2545 cm^{-1} is in agreement with a *closo* structure of the *o*-carboranyl fragment as is the $^{11}\text{B-NMR}$, which display a pattern of intensity resonances of 2:3:5 in the range $-3/-10\text{ ppm}$ in agreement with a C_{2v} symmetry. This implies that one of the aromatic rings of each phosphorus is above the mirror plane defined by the two phosphorus and the two cluster carbon atoms while the second is below. This plane also does contain the PdCl_2 fragment. To unambiguously proof the structure of this compound, a single crystal X-ray study was performed.

The carborane cage in $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$ is coordinated bidentately through P atoms to the Pd(II) ion. Two chloride ions at *cis* positions fulfil the slightly distorted square-planar coordination around the metal. A perspective view of the complex unit is given in Fig. 1 and selected bond lengths and angles are listed in Table 1. Pd–Cl distances (2.3453(14) and 2.3423(13) Å) are equal within experimental errors, as well as Pd–P distances (2.2325(13) and 2.2284(14) Å). Angles around Pd do not deviate much from values for a regular square-planar coordination geometry.

The bond lengths in the coordination sphere of $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$ agree well with the corresponding values in $[\text{PdCl}_2(\text{dppe})]\cdot\text{CH}_2\text{Cl}_2$ [4]; the Pd–P bonds are equal within experimental errors and the Pd–Cl distances are only slightly longer in the compared compound. The difference in the Pd–Cl distances probably originates from different *trans* influence of the P atoms. Also, as a matter of comparison, Pd–P and Pd–Cl distances in $[\text{PdCl}_2(1,2\text{-(PPhCl)}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot 2\text{THF}$ are both slightly shorter than in $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$ [5]. The difference can be explained by the electron-

withdrawing capacity of Cl atoms bonded to P in the former complex.

Comparison of configuration of the carborane ligand in $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$ and this in the free $1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ ligand reveals noticeable differences. In the free ligand the P1–C1–C2–P2 torsion angle is $-10.9(3)^\circ$ [6]. Moreover, the mutual orientations of the phenyl groups compared to the carborane cage are quite different, and thus, symmetry deviates markedly from C_{2v} . Coordination of the ligand to Pd(II) changes orientation of the phenyl groups considerably. Symmetry of the ligand in the complex, as well as that of the complex unit, in $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$ is approximately C_{2v} and the P1–C1–C2–P2 torsion angle is $0.4(3)^\circ$. In addition, due to coordination, the C1–C2 distance shortens from $1.722(4)$ Å in the free ligand to $1.695(5)$ Å in the complex.

It seems clear that avoiding nucleophilic agents the *closo* nature of the cage can be preserved. To proof so, we have used 'the safe' CH_2Cl_2 to synthesize $[\text{PdCl}_2(1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$. We had chosen the $\text{-P}^i\text{Pr}_2$ fragment to produce a more nucleophilic *o*-carboranyl-phosphine than $1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, and see if this had some effect on the deboronation of the complex.

The reaction of $1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ with $[\text{PdCl}_2(\text{cod})]$ was performed in CH_2Cl_2 as for $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$. As the ^{11}B -NMR demonstrated, the *closo* nature of the carborane cluster was preserved, and ^{11}B -NMR resonances in the range $0/-10$ ppm were found. Thus, a structure similar to that of $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ is expected.

^1H -NMR spectra indicates that in $[\text{PdCl}_2(1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ two methyl groups in each isopropyl group are not equivalent (Fig. 2). Two methyl groups appear at the same chemical shift but the coupling constants $^3J(\text{H,H})$ and $^3J(\text{P,H})$ are different. Their values are 6.9 and 24.1 Hz for one methyl group, and 11.7 and 7.1 Hz for the other one. The $^{13}\text{C}\{^1\text{H}\}$ spectrum shows two different resonances at 21.29 and 20.00 ppm, which agree and support two different methyl groups in each isopropyl group. Contrarily to the synthesis of $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$, a minor quantity of the deboronated species $[\text{Pd}_2(\mu\text{-Cl})_2\{7,8\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}_2]$ was obtained. Precise confirmation of the nature of $[\text{Pd}_2(\mu\text{-Cl})_2\{7,8\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}_2]$ was obtained by comparing the cell dimensions of obtained crystals with this of a pure sample [3c].

To know what effect a 'mild' nucleophile could produce in a hypothetical separation process, $[\text{PdCl}_2(1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ was refluxed for 5–10 min in acetonitrile. In this case $[\text{PdCl}_2(1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ and $[\text{Pd}_2(\mu\text{-Cl})_2\{7,8\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}_2]$ were obtained in comparable quantities, largely depending on the refluxing time. No attempt was made to separate this mixture as $[\text{Pd}_2(\mu\text{-Cl})_2\{7,8\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}_2]$ can be easily produced from $1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ and $[\text{PdCl}_2(\text{PhCN})_2]$ in deoxygenated ethanol, as was earlier reported [3c].

As a conclusion, we believe it is of outmost importance for producing pure samples of these C-substituted *closo* carboranyl compounds, to use dry non-nucleophilic solvents to perform the reaction, even avoiding

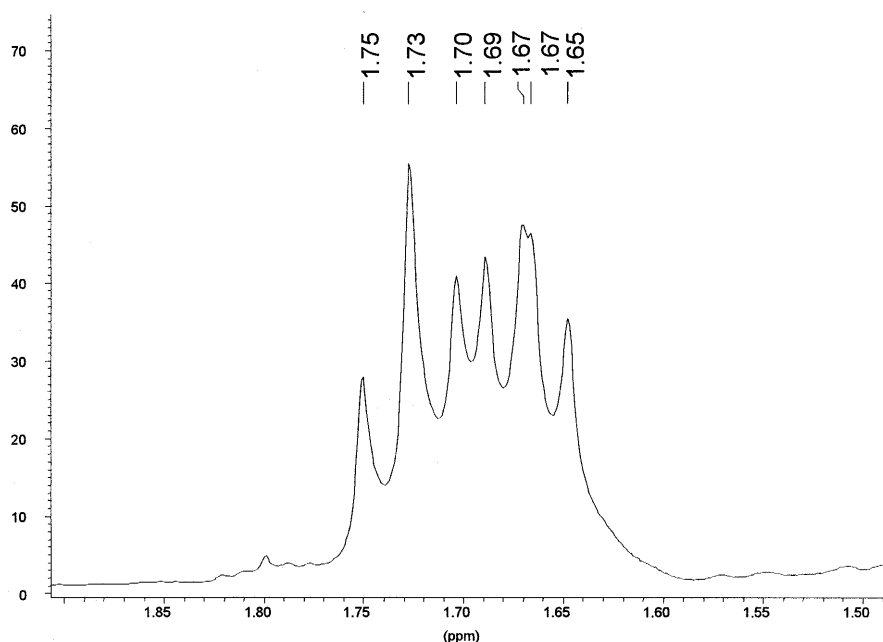


Fig. 2. Methyl signal region in the ^1H -NMR spectra of $[\text{PdCl}_2(1,2\text{-}(\text{P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$.

the eventual use of alcohols or nucleophilic agents in purification, which in more or less extent will produce deboronation of the cluster in the complex. We would also extend these precautions to the syntheses of other complexes already reported with transition metals other than Pd as it is most possible that the same problem occurs [7].

3. Experimental

3.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded with KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^1H - and $^1\text{H}\{^{11}\text{B}\}$ -NMR (300.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.47 MHz), $^{31}\text{P}\{^1\text{H}\}$ -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 $\text{BF}_3\cdot\text{OEt}_2$ and those for ^1H -, $^1\text{H}\{^{11}\text{B}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were referenced to SiMe_4 . Chemical shift values for $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were referenced to external 85% H_3PO_4 . Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hz.

3.2. Materials

Unless otherwise noted, all manipulations were carried out under a dinitrogen or argon atmosphere using standard vacuum line techniques. Diethyl ether and toluene were distilled from sodium benzophenone prior to use. Dichloromethane was dried over molecular sieves and deoxygenated prior to use, and the rest of the solvents were of reagent grade quality and were used without further purification. $[\text{PdCl}_2(\text{cod})]$ [8] and $[\text{PdCl}_2(\text{PhCN})]$ [9] were prepared according to the literature methods. $1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ [10] and $1,2\text{-(P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ [11] were synthesised by previously published methods.

3.3. Synthesis of $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ (method A)

A mixture of $1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (0.20 g, 0.39 mmol) and $[\text{PdCl}_2(\text{cod})]$ (0.11 g, 0.39 mmol) in dichloromethane (24 ml) was stirred at room temperature for 20 min prior refluxing for 24 h. The reaction mixture was cooled and filtered through Celite. The filtrate was dried in vacuo. The obtained solid was washed with diethyl ether and dried in vacuo (0.26 g, 96%). Anal. Calc. for $\text{C}_{26}\text{H}_{30}\text{B}_{10}\text{Cl}_2\text{P}_2\text{Pd}$: C, 45.26; H,

4.38. Found: C, 45.22; H, 4.30. IR: ν (cm^{-1}) = 3061 ($\text{C}_{\text{aryl}}\text{-H}$), 2615, 2624, 2545, 2580 (B-H), 1437, 1096, 1075, 686, 506 (phosphines). ^1H -NMR (CD_2Cl_2 , 25°C): δ = 8.26 (m, H_{aryl} , 8H), 7.72–7.68 (m, H_{aryl} , 4H), 7.63–7.58 (m, H_{aryl} , 8H), 3.25–1.17 (br, B-H). $^1\text{H}\{^{11}\text{B}\}$ -NMR (CD_2Cl_2 , 25°C): δ = 8.26 (m, H_{aryl} , 8H), 7.72–7.68 (m, H_{aryl} , 4H), 7.63–7.58 (m, H_{aryl} , 8H), 2.62 (br s, B-H , 2H), 2.44 (br s, B-H , 2H), 2.24 (br s, B-H , 2H), 2.08 (br s, B-H , 4H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 25°C): δ = 136.06 (m, $o\text{-C}_{\text{aryl}}$), 133.67 (s, $p\text{-C}_{\text{aryl}}$), 128.74 (m, $m\text{-C}_{\text{aryl}}$), 125.85 (d, $^1J(\text{C,P}) = 4.1$, $ipso\text{-C}_{\text{aryl}}$), 125.05 (d, $^1J(\text{C,P}) = 2.8$, $ipso\text{-C}_{\text{aryl}}$), 87.31 (t(1:1:1), $^1J(\text{C,P}) = 13.8$, $\text{C}_{\text{cluster}}$). ^{11}B -NMR (CD_2Cl_2 , 25°C): δ = –3.0 (d, 2B, $^1J(\text{B,H}) = 144$), –3.5 (d, 3B, $^1J(\text{B,H}) = 160$), –10.03 (5B). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 25°C): δ = 78.30 (s, PPh_2).

3.4. Synthesis of $[\text{PdCl}_2(1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ (method B)

A mixture of $1,2\text{-(PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (0.10 g, 0.20 mmol) and $[\text{PdCl}_2(\text{PhCN})_2]$ (0.077 g, 0.20 mmol) in toluene (10 ml) was refluxed for 24 h. After filtration the solid was washed with dichloromethane until the washing solution was colourless. Clear solution was obtained by filtration through Celite. The filtrate was concentrated in vacuo. Layering with petroleum ether precipitated solid product (0.09 g, 64%). Characterization was as for method A.

3.5. Synthesis of $[\text{PdCl}_2(1,2\text{-(P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$

$1,2\text{-(P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (0.10 g, 0.27 mmol) and $[\text{PdCl}_2(\text{cod})]$ (0.077 g, 0.27 mmol) were dissolved in dichloromethane (12 ml). The mixture was refluxed for 24 h. The solvent was evaporated and the obtained solid was washed with diethyl ether and dried in vacuo (0.42 g, 96%). Anal. Calc. for $\text{C}_{14}\text{H}_{38}\text{B}_{10}\text{Cl}_2\text{P}_2\text{Pd}$: C, 30.36; H, 6.92. Found: C, 30.88; H, 6.88. IR (KBr): ν (cm^{-1}) = 2993, 2931, 2875 (C-H (P^iPr)), 2636, 2576 (B-H), 1455, 1386, 1249, 1074, 1040, 877, 657, 638, 505 (phosphine). ^1H -NMR (CD_2Cl_2 , 25°C): δ = 1.70 (dd, $^3J(\text{H,H}) = 6.9$, $^3J(\text{P,H}) = 24.1$, 12H), 1.70 (dd, $^3J(\text{H,H}) = 11.7$, $^3J(\text{P,H}) = 7.1$, 12H), 2.10–2.08 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 25°C): δ = 86.58 ($\text{C}_{\text{cluster}}$), 31.86 (d, $^1J(\text{C,P}) = 9.7$, P-CH), 31.72 (d, $^1J(\text{C,P}) = 9.7$, P-CH), 21.29 (s, CH_3), 20.00 (s, CH_3). $^{11}\text{B}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 25°C): δ = –0.4 (d, $^1J(\text{B,H}) = 83$, 2B), –3.4 (d, $^1J(\text{B,H}) = 153$, 2B), –9.9 (d, $^1J(\text{B,H}) = 153$, 6B). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 25°C): δ = 69.10 (s, P^iPr_2).

3.6. Synthesis of $[\text{Pd}_2(\mu\text{-Cl})_2\{7,8\text{-(P}^i\text{Pr}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}_2]$

$[\text{PdCl}_2(1,2\text{-(P}^i\text{Pr}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]$ produced as above was refluxed in acetonitrile for 5–10 min. The mixture

Table 2
Crystallographic data for $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$

Empirical formula	$\text{C}_{27}\text{H}_{32}\text{B}_{10}\text{Cl}_4\text{P}_2\text{Pd}$
Formula weight	774.77
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	12.312(4)
b (Å)	13.797(4)
c (Å)	10.999(5)
α (°)	110.58(2)
β (°)	99.45(3)
γ (°)	86.36(3)
V (Å ³)	1725.4(11)
Z	2
D_{calc} (g cm ⁻³)	1.491
μ (cm ⁻¹)	9.61
Number of unique reflections	6239
Number of parameters	397
Goodness-of-fit on F^2	1.061
$R_1(F_o)^a$ [$I > 2\sigma(I)$]	0.0478
$wR_2(F_o^2)^b$ [$I > 2\sigma(I)$]	0.1290
Largest differential peak and hole (e Å ⁻³)	1.63 and -1.68 ^c

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

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

^c Peak coordinates $x = 0.3896$; $y = 0.1762$; $z = 0.1825$ (1.02 Å from Pd); hole coordinates $x = 0.3808$; $y = 0.2091$; $z = 0.1446$ (0.95 Å from Pd).

was filtered and the filtrate was dried in vacuo giving a yellow–brown solid. Crystals were obtained from $\text{CHCl}_3\text{--CH}_2\text{Cl}_2$ (layering). Anal. Calc. for $\text{C}_{14}\text{H}_{38}\text{B}_9\text{ClP}_2\text{Pd}$: C, 33.13; H, 7.54. Found: C, 33.16; H, 7.29. All other characterization was in agreement with literature data [3c].

3.7. X-ray crystallographic study

Yellow crystals of $[\text{PdCl}_2(1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})]\cdot\text{CH}_2\text{Cl}_2$ were grown from dichloromethane–*n*-hexane. Single-crystal data collection was performed at -80°C on a Rigaku AFC7S diffractometer using graphite monochromatized Mo– K_α radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centred reflections. A total of 6552 reflections, giving 6239 independent reflections ($R_{\text{int}} = 0.0273$) were collected by $\omega/2\theta$ scan mode ($2\theta_{\text{max}} = 50.5^\circ$). The data obtained were corrected for Lorentz and polarization effects. Correction for empirical absorption (ψ scan) was also applied. The structure was solved by direct methods and refined by full-matrix least squares on F^2 techniques using the SHELX-97 program package [12]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and

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. Experimental parameters are listed in Table 2.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139282. Copies of this information may be obtained free of charge from The Director, 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).

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References

- [1] W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143.
- [2] J.S. Kim, J.H. Pawlow, L.M. Wojcinski II, S. Murtuza, S. Kacker, A. Sen, J. Am. Chem. Soc. 120 (1998) 1932.
- [3] (a) F. Teixidor, C. Viñas, M.M. Abad, M. Lopez, J. Casabó, Organometallics 12 (1993) 3766. (b) F. Teixidor, C. Viñas, M.M. Abad, C. Whitaker, J. Rius, Organometallics 15 (1996) 3154. (c) C. Viñas, M.M. Abad, F. Teixidor, R. Sillanpää, R. Kivekäs, J. Organomet. Chem. 555 (1998) 17.
- [4] W.L. Steffen, G.J. Palenik, Inorg. Chem. 15 (1976) 2432.
- [5] V.P. Balema, S. Blaurock, V.K. Pecharsky, E.G. Rys, E. Hey-Hawkins, Polyhedron 17 (1998) 3771.
- [6] S. Paavola, R. Kivekäs, C. Viñas (unpublished results).
- [7] (a) W.E. Hill, W. Levason, C.A. McAuliffe, Inorg. Chem. 13 (1974) 244. (b) L.I. Zakharkin, G.G. Zhigareva, Izv. Akad. Nauk. SSSR Ser. Khim. (1965) 932; Chem. Abst. 63 (1965) 5673g. (c) H.D. Smith Jr., J. Am. Chem. Soc. 87 (1965) 1817. (d) G. Allender, H.D. Smith Jr., Inorg. Chim. Acta 26 (1978) L38. (e) W.E. Hill, B.G. Rackley, L.M. Silva-Trivino, Inorg. Chim. Acta 75 (1983) 51. (f) J.G. Contreras, L.M. Silva-Triviño, M.E. Solis, Inorg. Chim. Acta 114 (1986) 51. (g) M. Kumada, K. Sumitani, Y. Kiso, K. Tamao, J. Organomet. Chem. 50 (1973) 319. (h) M.E. Solis, M.S. Trivino, J.G. Contreras, Bol. Soc. Chil. Quim. 27 (1982) 88; Chem. Abst. 97 (1982) 103204b.
- [8] D. Drew, J.R. Doyle, Inorg. Synth. 28 (1990) 346.
- [9] J.R. Doyle, P.E. Slade, H.B. Jonassen, Inorg. Synth. 6 (1960) 216.
- [10] R.P. Alexander, H. Schroeder, Inorg. Chem. 2 (1963) 1107.
- [11] F. Teixidor, C. Viñas, M.M. Abad, R. Nuñez, R. Kivekäs, R. Sillanpää, J. Organomet. Chem. 503 (1995) 193.
- [12] G.M. Scheldrick, SHELX-97, Universität Göttingen, Göttingen, Germany, 1997.