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Reactions of Pd(II) with *closo*-1,2-dicarbadodecaborane-1,2-diphosphines

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Abstract

The reactivity of carboranyldiphosphines towards palladium (II) complexes and the modifications that take place on the cluster are studied in this work. The reaction of aryl, alkyl or alkoxy substituted *closo*-carboranyldiphosphines with palladium (II) complexes [$PdCl_2L_2$] (L = PPh_3, $PMePh_2$, PhCN) in ethanol, yields products in which partial degradation of the carborane cage has taken place and total or partial substitution of the chlorine atoms of the initial palladium (II) complex has been observed. The final stoichiometry depends on the steric characteristics of the ligand, their basicity and the starting Pd(II) complex. The crystal structure of [$Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2Bq_9H_{10}\}_2$] the third structurally characterized example of a bis chloride bridged palladium complex with phosphines has been determined.

Keywords: Carboranes; Diphosphines; Degradation; Chloride-bridged

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1. Introduction

The influence of 7,8-dicarba-*nido*-undecaborate(1 −) on the coordinating behavior of electron-rich elements such as sulphur [1,2] and phosphorus [3] has been of interest to us. Currently we are studying the reactivity of *nido* carboranyldiphosphines, such as [$7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}$]$^-$, [$7,8\text{-}(PEt_2)_2\text{-}7,8\text{-}C_2B_9H_{10}$]$^-$, [$7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}$]$^-$, and [$7,8\text{-}(P\{OEt\}_2)_2\text{-}7,8\text{-}C_2B_9H_{10}$]$^-$. Although complexes of 1,2-bis (diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane [$1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$] with transition metals such as nickel(II) [4], cobalt(II) [5], gold(I) [6], platinum(II) [7], palladium(II) [8], chromium, molybdenum, tungsten, iron [9] and manganese [10], and those of [$1,2\text{-}(PEt_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$] with Ni(0) [11] have been reported, only few preceding papers [12] deal with the anion [$7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}$]$^-$. This kind of new anionic diphosphines exhibit some similarities to the popular 1,2-diphenylphosphinoethane (diphos), however the differences are notorious, and dissimilar ligating properties are expected [12]b. The reasons for the differences are the anionic charge of the new diphosphines, their eclipsed conformation, and the possible participation of the B(3)–H vertex in the coordination to the metal as it has been observed in [$7,8\text{-}(SR)_2\text{-}7,8\text{-}C_2B_9H_{11}$]$^-$ complexes [13].

Here we report on the reactivity of these ligands towards Pd(II) and the molecular structure of [$Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2$], which to the best of our knowledge is the third structurally characterized example of a bis chloride bridged palladium complex with phosphines [14].

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2. Results and discussion

The reaction of aryl, alkyl or alkoxy substituted *closo*-carboranyldiphosphines with $[PdCl_2(PPh_3)_2]$, $[PdCl_2(PhCN)_2]$ or $[PdCl_2(PMePh_2)_2]$, in ethanol, yields complexes in which partial degradation of the carborane cage has taken place. In addition partial or total substitution of the chlorine atoms of the starting Pd(II) complex has been found.

The partial degradation by the complexation method had already been disclosed [12], and it implies the reaction of the *closo* species with transition metal complexes in ethanol. By partial degradation it is understood the removal of one formally B^+ fragment from the *closo* species (C_2B_{10} cluster) to yield the *nido* species ($C_2B_9^-$ cluster). Many transition metal complexes lead to partial degradation, but the dicharged metallic cations seem to be the most appropriated ones for this process.

The hydrogen bridge resonance in the ^1H-NMR spectrum at approx. $\delta = -2.7$ ppm, and the ^{11}B-NMR patterns (2:3:2:1:1 or variation of this caused by accidental overlap of the bands or from the lack of symmetry) in the range between -8 and -37 ppm indicates that the ligand's original *closo* cluster is not retained upon coordination, and that partial degradation has taken place. Thus the resonance at δ ca. -2.7 ppm provides information on the cluster's charge, and indeed on the presence or absence of the open face hydrogen bridge. The lack of any absorption at higher field values than -2.7 ppm in the ^1H-NMR spectrum rules out any $B(3){-}H \rightarrow M$ interaction [15]. As a result we hypothesize that the metal atom is only coordinated to the two phosphorus groups of $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Ph, Et, ^{i}Pr, OEt) while the other two coordination positions are occupied by Cl^- and L (L = PPh_3 or $PMePh_2$), a second ligand $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ or two Cl^- bridges. The metal's charge and the coordination number are satisfied in this way.

The substitution of one or two chlorine atoms is not well understood, although it seems to be a compromise of the basicity of the phosphine, the steric characteristics of the ligand, and the solubility of the formed species. Equations below exemplify these reactions.

$$1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10} + [PdCl_2L_2] \xrightarrow{\text{Ethanol}} [PdCl(7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10})L] + \text{other} \quad (1)$$

(L = PPh_3, R = Ph, Et; or L = $PMePh_2$, R = Ph)

$$2\,(1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}) + [PdCl_2(PhCN)_2] \xrightarrow{\text{Ethanol}} [Pd(7,8\text{-}(PR_2)_2 - 7,8\text{-}C_2B_9H_{10})_2] + \text{other} \quad (2)$$

(R = Ph, Et)

$$2\,(1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}) + [PdCl_2(PhCN)_2] \xrightarrow{\text{Ethanol}} [PdCl(7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10})]_2 + \text{other} \quad (3)$$

(R = ^{i}Pr, OEt)

In every case the resulting complexes contain the partially degraded species 7,8-diphosphine-7,8-dicarba-*nido*-undecaborate (1 −). The stoichiometry $[PdCl(7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$, which means substitution of a chlorine atom and a PPh_3 group by the anionic diphosphine generated in situ, is found for all the ligands (R = Ph, Et, ^{i}Pr, OEt) when the starting Pd(II) complex is $[PdCl_2(PPh_3)_2]$ (Eq. (1)). The low solubility of these complexes in common solvents did not allow to complete their NMR characterization. A better characterization was possible when $[PdCl_2(PMePh_2)_2]$ was utilized to produce the new $[PdCl(7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PMePh_2)]$ compounds. Although they precipitate out of the solution (ethanol), the solubility of the complexes is high enough to allow their complete NMR characterization.

The reaction of $[1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ with $[PdCl_2(PhCN)_2]$ in a 2:1 ratio yielded complexes with the stoichiometry $[ML_2]$ and $[MClL]_2$. The complex $[ML_2]$ is obtained for L = $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and $[7,8\text{-}(PEt_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. For L = $[7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ or $[7,8\text{-}(P\{OEt\}_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ the new complex $[MClL]_2$ is obtained. The two weakly coordinating ligands PhCN are always displaced, but one or both chlorine ligands can be substituted. One of the most intriguing features about the reactivity of this kind of ligands is the variety of observed stoichiometries. All ligands have identical coordinating elements placed in the same position with respect to the carborane cage. The only differences are the steric hindrance and the basicity of the R groups bonded to each phosphorus. It is interesting to notice that by considering only steric effects, some of these stoichiometries can be predicted. With bulky ligands such as $[7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ compounds with a ligand:metal ratio 1:1 could be expected. In a 2:1 ratio high steric crowding would be expected in a square planar arrangement. With ligands such as $[7,8\text{-}(PEt_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$, the steric hindrances are minor and a ratio 2:1 is possible. The seemingly exceptions of the bulky $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ which leads to $[ML_2]$ and the non bulky $[7,8\text{-}(P\{OEt\}_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ which leads to $[MClL]_2$ may indicate, however, that there is another important factor which has an important role in determining the type of stoichiometry: the basicity of the ligands.

The X-ray crystal structure of $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ clearly confirms the *nido* nature of the cage and the dinuclear character of the complex. The crystal data and selected bonding parameters for

$[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ are presented in Tables 1 and 2. An ORTEP plot of the dinuclear unit is presented in Fig. 1. The molecule situates across the center of inversion at 0,0,1/2, but the real molecule in the structure is not centrosymmetric. The structure is partly disordered with the Pd and Cl atoms occupying two different positions (A and B) and having population parameters 0.5. This kind of disorder is rarely seen with heavy atoms and it means that if the Pd atom is at the position Pd(1A) there is no Pd atom at the position Pd(1B), but there is an Pd atom at $Pd(1B)^i$ ($i = -x, -y, 1-z$), and so on. In that way each Pd atom in the dimer gets a square-planar geometry with two Pd–P and two Pd–Cl bonds. Thus each Pd atom has two different orientations with respect to the open face of the carborane moiety. Pd(1A) deviates 0.618(7) Å from the plane through the atom group P(1)C(7)C(8)P(2), but Pd(1B) is approximately at the plane deviating only − 0.024(7) Å. If the metal atom occupies Pd(1A), and since it is *anti* with respect to the open face of the carborane at *x*, *y*, *z*, then the second Pd atom of the molecule, $Pd(1B)^i$, situates approximately at the plane through the atom group $P(1)^iC(7)^iC(8)^iP(2)^i$. The Pd–P bonds are unsymmetrical, Pd(1A)–P(1) and Pd(1A)–P(2) are 2.275(3) and 2.201(3) Å, respectively. In the mononuclear complex [16] $[o\text{-}C_6H_4(^iPr_2P)_2]PdCl_2$ the Pd–P distances are almost identical being 2.234(1) and 2.233(1) Å, while in the dinuclear complex $[Pd_2(\mu\text{-}Cl)_2\{(P(OEt)_2O)_2H\}_2]$ the Pd–P bond distances are 2.207(2) and 2.233(2) Å [17]. This means that unsymmetry in Pd–P bonds is due to the Pd–Cl–Pd bridge system. The phosphine ligand in $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ is bulky and rigid. Thus the centrosymmetric chlorobridges which form the square-planar coordination sphere for Pd(II) cation can not be formed. The Pd–Cl bonds range from 2.396(5) to 2.416(5) Å, which are slightly longer than those of 2.387(2) and 2.398(2) Å found in $[Pd_2(\mu\text{-}Cl)_2\{(P(OEt)_2O)_2H\}_2]$.

Table 1
Crystallographic data for $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

Chem formula	$C_{28}H_{76}B_{18}Cl_2P_4Pd_2$
f_w	1015.05
a	8.664 (1) Å
b	19.949 (3) Å
c	14.555 (2) Å
β	100.98 (2)°
V	2469.7 (7) Å^3
Z	4
Space group	Monoclinic, $P21/n$ (# 14)
T	23°C
λ(MoKα)	0.71069 Å
ρ_c	1.365 g cm^{-3}
μ	9.78 cm^{-1}
Transm. coeff.	0.91–1.00
$R(F_o)$	0.061
$R_w(F_o)$	0.071

Table 2
Selected interatomics distances (Å) and angles (°) with Esd's in parentheses for $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

Distances	
Pd(1A)–Cl(1A)	2.405(5)
Pd(1A)–Cl(1B^i)	2.407(5)
Pd(1A)–P(1)	2.275(3)
Pd(1A)–P(2)	2.201(3)
Pd(1B)–Cl(1A^i)	2.396(5)
Pd(1B)–Cl(1B)	2.416(5)
Pd(1B)–P(1)	2.230(3)
Pd(1B)–P(2)	2.316(3)
P(1)–C(2)	1.91(1)
P(1)–C(5)	1.82(1)
P(1)–C(7)	1.829(7)
P(2)–C(8)	1.824(7)
P(2)–C(10)	1.85(1)
P(2)–C(13)	1.84(1)
C(7)–C(8)	1.575(9)
Angles	
Cl(1A)–Pd(1A)–Cl(1B^i)	83.0(2)
Cl(1A)–Pd(1A)–P(1)	94.0(2)
Cl(1A)–Pd(1A)–P(2)	177.8(2)
Cl(1Bi)– Pd(1A)–P(1)	176.8(2)
Cl(1Bi)– Pd(1A)–P(2)	95.9(2)
P(1)–Pd(1A)–P(2)	87.0(1)
Cl(1B)–Pd(1B)–Cl(1A^i)	83.0(2)
Cl(1B)–Pd(1B)–P(1)	97.0(2)
Cl(1B)–Pd(1B)–P(2)	177.5(2)
Cl(1Ai)– Pd(1B)–P(1)	178.6(2)
Cl(1Ai)– Pd(1B)–P(2)	94.7(2)
P(1)–Pd(1B)–P(2)	85.4(1)
Pd(1A)–Cl(1A)–Pd(1B^i)	95.4(2)
Pd(1B)–Cl(1B)–Pd(1A^i)	94.9(2)
Pd(1A)–P(1)–C(2)	116.2(4)
Pd(1A)–P(1)–C(5)	109.3(4)
Pd(1A)–P(1)–C(7)	108.2(2)
Pd(1B)–P(1)–C(2)	99.1(4)
Pd(1B)–P(1)–C(5)	119.9(4)
Pd(1B)–P(1)–C(7)	114.1(2)
C(2)–P(1)–C(5)	112.7(6)
C(2)–P(1)–C(7)	103.1(4)
C(5)–P(1)–C(7)	106.7(4)
Pd(1A)–P(2)–C(8)	110.0(2)
Pd(1A)–P(2)–C(10)	119.7(3)
Pd(1A)–P(2)–C(13)	105.5(4)
Pd(1B)–P(2)–C(8)	111.8(2)
Pd(1B)–P(2)–C(10)	104.1(3)
Pd(1B)–P(2)–C(13)	117.9(4)
C(8)–P(2)–C(10)	106.1(4)
C(8)–P(2)–C(13)	112.2(5)
C(10)–P(2)–C(13)	103.3(7)
P(1)–C(7)–C(8)	114.2(4)
P(2)–C(8)–C(7)	114.6(4)

The partial degradation upon coordination of the *closo* ligands was initially attributed to transfer of electron density from the metal to the cage by Cc–P–M coordination [12], which leads to opening of the cage. In such a situation the apical boron atom would be more loosen, and susceptible to nucleophilic attack. Ethanol is a suitable nucleophile to bring about this

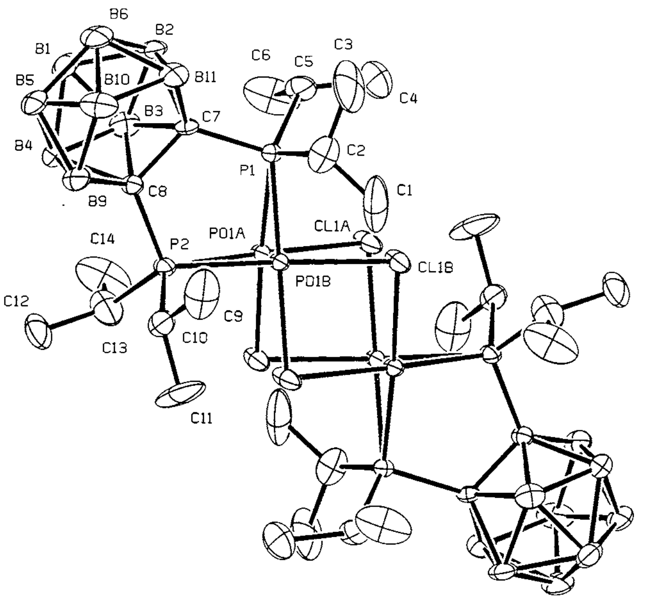

Fig. 1. ORTEP plot of $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$. Thermal ellipsoids are shown at 30% probably levels. The H atoms are omitted for clarity.

partial degradation. Recently, last results in our group seem to indicate that the factor influencing the partial degradation may be the opposite. Electron density is dissipated from the cage by Cc–P–M bonds for a diphosphine ligand derivative (Fig. 2), or Cc–S–M bonds for a dithio one. Those indications are based on the measurements of the E^0 value in metallocarboranes containing Cc–S bonds [18], and by easy formation of phosphonium substituted carboranes by P–H or P–I bonds [3,19].

As a conclusion, the *nido* carboranyldiphosphines react with Pd(II) complexes in the following way: i) partial degradation of the cage takes place upon complexation, ii) the new anionic diphosphine generated in situ produces the substitution of one anionic and one neutral group (e.g. Cl^- and PPh_3) or two groups, depending on their coordinating ability. The main apparent difference between the ligands is the steric hindrance, which could justify the observed stoichiometries, but other differences such as basicity or electronic effects could be of great importance in determining the stoichiometry.

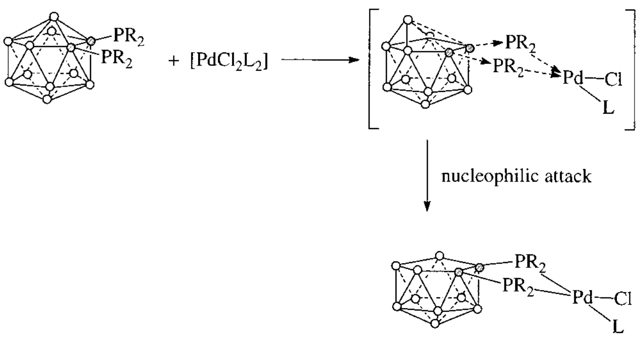

Fig. 2. Proposed mechanism for the partial degradation of 1,2-diphosphine-*o*-carborane derivatives in the complexation with $[PdCl_2L_2]$ (L = PPh_3, $PMePh_2$, PhCN) in ethanol.

3. Experimental section

3.1. General methods

Before use, 1,2-dicarba-*closo*-dodecaborane (Dexsil) was sublimed; 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane, 1,2-bis(diethylphosphino)-1,2-dicarba-*closo*-dodecaborane, 1,2-bis(diisopropyl-phosphino)-1,2-dicarba-*closo*-dodecaborane and 1,2-bis-(dietoxyphosphino)-1,2-dicarba-*closo*-dodecaborane were prepared from 1,2-dicarba-*closo*-dodecaborane according to the literature [3]. A 1.6 M solution of *n*-butyllithium in hexane from Fluka was used as purchased. $[PdCl_2(PPh_3)_2]$ [20], $[PdCl_2(PMePh_2)_2]$ [21] and $[PdCl_2(PhCN)_2]$ [22] were synthesized as described.

All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as purchased. The solvents were reagent grade. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed in our analytical laboratory by using a Perkin–Elmer 240B microanalycer. IR spectra were measured on a Nicolet 710-FT espectrophotometer. The ^{1}H-NMR, ^{11}B-NMR and ^{31}P-NMR spectra were recorded on a Bruker AM 400WB or AC 250WB instruments. Chemical shift data relative to TMS in the ^{1}H-RMN spectra and to $Et_2O \cdot BF_3$ in the $^{11}B\{^1H\}$-RMN and ^{11}B-RMN spectra (minus values upfield) are given in ppm, followed by a description of the multiplet (e.g. d = doublet), its relative intensity and observed coupling constants given in Hz. Chemical shift data relative to H_3PO_4 in the $^{31}P\{^1H\}$-RMN spectra (positive values downfield) are given in ppm.

3.2. Preparation of $[PdCl\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(PPh_3)]$

$[PdCl_2(PPh_3)_2]$ (70 mg, 0.099 mmol) was added to a slurry of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (50 mg, 0.099 mmol) in deoxygenated ethanol (15 ml). The yellow slurry was refluxed for 3 h and then solids were filtered, washed with hot ethanol, and dried in vacuum to afford 62 mg yellow compound (yield 70%). Anal. calcd. for $C_{44}H_{45}B_9P_3ClPd$: C, 58.34; H, 5.01. Found: C, 58.89; H, 4.88. IR (KBr): ν [cm^{-1}] = 2592, 2548 (B–H). ^{1}H-NMR in acetone d_6: δ −2.4 (br, 1H, B*H*B), 7.43–7.70, 7.17–7.25 (m, 35H, C_{aryl}-*H*). $^{11}B\{^1H\}$-NMR in acetone: $\delta = -8.3$ (1B), −10.5 (2B), −14.0 (2B), −16.7 (2B), −26.9 (1B), −34.2 (1B).

3.3. Preparation of $[PdCl\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(PMePh_2)]$

$[PdCl_2(PMePh_2)_2]$ (54 mg, 0.104 mmol) was added to a solution of of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (52 mg, 0.104 mmol) in hot deoxygenated ethanol (15 ml) and the mixture was refluxed for 2 h. Then, the yellow solid was filtered off, washed with warm ethanol and dried on a vacuum line to yield microcrystalline $[PdCl\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(PMePh_2)]$ (55 mg, 65%). Anal. calcd. for $C_{39}H_{43}B_9P_3ClPd$: C, 55.51; H, 5.14. Found: C, 55.46; H, 5.29. FTIR (KBr): ν [cm^{-1}] = 2574, 2557, 2536 (B–H). ^{1}H-NMR in acetone d$_6$: δ −2.5 (br, 1H, B*H*B), 1.66–1.69 (m, 3H, C*H*$_3$), 7.15–7.20, 7.27–7.63 (m, 20H, C$_{\text{aryl}}$-*H*), 7.81–7.86, 8.01–8.06 (m, 10H, C$_{\text{aryl}}$-*H*). ^{11}B-NMR in CD_2Cl_2: $\delta = -9.5$ (1B), −10.8 (1B), −12.2 (2B), −15.5 (d, 3B, ^1J(B,H) = 119 Hz), −27.7 (1B), −35.0 (d, 1B, ^1J(B,H) = 140 Hz). ^{31}P{^{1}H}-NMR in CD_2Cl_2: $\delta = 8.70$ (dd, ^2J(P,P) = 17 Hz, ^2J(P,P) = 412 Hz, *P*MePh$_2$), 81.39 (t, ^2J(P,P) = 17 Hz, *P*Ph$_2$ with two P atoms in *cis*), 85.83 (dd, ^2J(P,P) = 17 Hz, ^2J(P,P) = 412 Hz, *P*Ph$_2$ trans to PMePPh$_2$).

3.4. Preparation of $[Pd\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

$[PdCl_2(PhCN)_2]$ (23 mg, 0.060 mmol) was added to a refluxing solution of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (60 mg, 0.119 mmol) in deoxygenated ethanol (20 ml). The solution was refluxed for 3 h and a yellow solid precipitated. This was filtered, washed with hot ethanol and dried on a vacuum line. After recrystallization in acetone/diethyl ether a yellow compound was obtained (34 mg, 51%). Anal. calcd. for $C_{52}H_{60}B_{18}P_4Pd$: C, 56.27; H, 5.45. Found: C, 54.38; H, 5.27. IR (KBr): ν [cm^{-1}] = 2541 (B–H). ^{1}H-NMR in acetone d$_6$: δ −2.7 (br, 2H, B*H*B), 7.73–7.77, 6.83–7.22 (m, 40H, C$_{\text{aryl}}$-*H*). ^{11}B-NMR in acetone: $\delta = -9.6$ (d, 4B, ^1J(B,H) = 131 Hz), −14.5 (d, 10B, ^1J(B,H) = 136 Hz), −28.1 (d, 2B, ^1J(B,H) = 108 Hz), −35.0 (d, 2B, ^1J(B,H) = 142 Hz). ^{31}P{^{1}H}-NMR in acetone: $\delta = 89.33$ (s).

3.5. Preparation of $[PdCl\{7,8\text{-}(PEt_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}(PPh_3)]$

$[PdCl_2(PPh_3)_2]$ (110 mg, 0.157 mmol) was added to a refluxing solution of $1,2\text{-}(PEt_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (50 mg, 0.156 mmol) in deoxygenated ethanol (20 ml). The yellow slurry was refluxed for 4 h and then the solids were filtered and washed with hot ethanol. The yellow solution yielded on cooling a pale microcrystalline solid, which was separated by filtration, washed with cool ethanol and dried in vacuum to afford 60 mg (yield 55%). Anal. calcd. for $C_{28}H_{45}B_9P_3ClPd$: C, 48.49; H, 3.63. Found: C, 47.88; H, 3.25. IR (KBr): ν [cm^{-1}] = 2544, 2531 (B–H). ^{1}H-NMR in CD_2Cl_2: δ −2.7 (br, 1H, B*H*B), 0.84–0.93, 1.15–1.50 (m, 12H, C*H*$_3$), 1.91–2.06, 2.17, 2.32–2.40 (m, 8H, C*H*$_2$), 7.42–7.64 (m, 15H, C$_{\text{aryl}}$-*H*). ^{11}B-NMR in CD_2Cl_2: $\delta = -14.0$ (d, 2B, ^1J(B,H) = 126 Hz), −19.8 (3B), −22.2 (2B), −31.9 (d, 1B, ^1J(B,H) = 104 Hz), −37.3 (d, 1B, ^1J(B,H) = 143 Hz). ^{31}P{^{1}H}-NMR in CD_2Cl_2: $\delta = 20.07$ (dd, ^2J(P,P) = 20 Hz and ^2J(P,P) = 380 Hz, *P*Ph$_3$), 89.86 (d, ^2J(P,P) = 20 Hz, *P*Et$_2$ *cis* to PPh$_3$), 96.87 (d, ^2J(P,P) = 380 Hz, *P*Et$_2$ trans to PPh$_3$).

3.6. Preparation of $[Pd\{7,8\text{-}(PEt_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

$[PdCl_2(PhCN)_2]$ (75 mg, 0.195 mmol) was added to a hot solution of $1,2\text{-}(PEt_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (125 mg, 0.390 mmol) in deoxygenated ethanol (25 ml). The mixture was refluxed for 2 h. The resulting grey solid was filtered off and the yellow solution was evaporated to dryness and dissolved in dichloromethane (5 ml). By addition of heptane (3 ml) and cooling, yellow product was formed, filtered, washed with a mixture of dichloromethane/heptane (1:4), and dried in vacuum to yield 75 mg (53%). Anal. calcd. for $C_{20}H_{60}B_{18}P_4Pd$: C, 32.95; H, 8.30. Found: C, 32.65; H, 8.04. IR (KBr): ν [cm^{-1}] = 2553 (B–H). ^{1}H-NMR in $CDCl_3$: δ −2.8 (br, 2H, B*H*B), 1.16–1.32 (m, 24H, C*H*$_3$), 2.09–2.15 (m, 16H, C*H*$_2$). ^{11}B-NMR in $CDCl_3$: $\delta = -8.5$ (d, 4B, ^1J(B,H) = 120 Hz), {−13.5, −16.0 (d, ^1J(B,H) = 160 Hz), 10B}, −26.2 (d, 2B, ^1J(B,H) = 144 Hz), −32.5 (d, 2B, ^1J(B,H) = 160 Hz). ^{31}P{^{1}H}-NMR in $CDCl_3$: $\delta = 71.73$ (s).

3.7. Preparation of $[Pd_2(\mu\text{-}Cl)_2\text{-}\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

$[PdCl_2(PhCN)_2]$ (51 mg, 0.133 mmol) was added to a refluxing solution of $1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (100 mg, 0.266 mmol) in deoxygenated ethanol (15 ml). The orange solution was refluxed for 2 h and the grey solid was filtered off. The solution was evaporated to dryness and dissolved in dichloromethane (5 ml). By addition of heptane (3 ml) and cooling, a yellow microcrystalline compound was separated, filtered, washed with a mixture of dichloromethane/heptane (1:4), and dried in vacuum to yield 72 mg (54%). A yellow crystal suitable for X-Ray analysis was grown from a dichloromethane/heptane solution (4:1) after partial evaporation of the solvent. When the ratio carborane/Pd(II) is 1:1 and the reaction conditions are the same, the same product is obtained but the yield drop below 31%. Anal. calcd. for $C_{14}H_{38}B_9P_2PdCl$: C, 33.27; H, 7.58. Found: C, 33.16, H, 7.29. IR (KBr): ν [cm^{-1}] = 2550 (B–H). ^{1}H-NMR in CD_2Cl_2: δ −2.8 (br, 2H, B*H*B), 1.41–1.52 (m, 48H, C*H*$_3$), 2.61–2.73 (m, 8H, C*H*$_2$). ^{11}B{^{1}H}-NMR in CD_2Cl_2: $\delta = -8.1$ (4B), {−13.1, −16.5, (10B}, −26.2 (2B), −30.9 (2B). ^{31}P{^{1}H}-NMR in CD_2Cl_2: $\delta =$ 121.76 (s).

3.8. Preparation of $[Pd_2(\mu\text{-}Cl)_2\text{-}\{7,8\text{-}(P\{EtO\}_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

$[PdCl_2(PhCN)_2]$ (26 mg, 0.069 mmol) was added to a hot solution of $1,2\text{-}(P\{OEt\}_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (53 mg, 0.138 mmol) in deoxygenated ethanol (20 ml). The orange solution was refluxed for 1 h and then the resulting grey solid was filtered. The solution was evaporated to dryness and dissolved in dichloromethane (5 ml). By addition of heptane (3 ml) and cooling, orange microcrystalline product was formed, filtered off, washed with a mixture of dichloromethane/heptane (1:4), and dried in vacuum to yield 35 mg (46%). When the ratio carborane/Pd(II) is 1:1 and the reaction conditions are the same, the same product is obtained but the reduction from Pd(II) to Pd(O) is higher and the yield drop below 28%. Anal. Calcd for $C_{10}H_{30}B_9P_2O_4PdCl$: C, 21.98; H, 5.53. Found: C, 22.25, H, 5.55. IR (KBr): $\nu\ [cm^{-1}] = 2550$ (B–H). ^1H-NMR in CD_2Cl_2: $\delta\ -2.8$ (br, 1H, BHB), 1.26–1.52 (m, 24H, CH_3), 4.26–4.34 (m, 16H, CH_2). $^{11}B\{^1H\}$-NMR in CD_2Cl_2: $\delta = -8.1$ (4B), -12.9 (4B), -17.7 (6B), -25.7 (2B), -33.0 (2B). $^{31}P\{^1H\}$-NMR in CD_2Cl_2: $\delta = 154.01$ (s).

3.9. X-Ray Structure Determination of $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$

Single crystal data collection was performed with Rigaku AFC5S diffractometer using monochromatized Mo-K_α radiation ($\lambda = 0.71069$ C). The scan mode was ω-2θ. The unit cell parameters were determined by least-squares refinements of 25 carefully centered reflections ($32° < 2\theta < 39°$). The data obtained were corrected for Lorentz and polarization effects and for dispersion. Also a correction for empirical absorption (ψ scan) was applied. A total of 6220 reflections were collected ($2\theta_{max} = 55°$), giving 5847 unique reflections ($R_{int} = 0.027$). Of those 2944 were considered as observed according the criteria $I > 3\sigma(I)$. The three check reflections monitored after every 150 reflections showed no decay during the course of the data collection.

The structure was solved by direct methods using MITRIL [23]. Least-squares refinements and all subsequent calculations were performed using the TEXSAN [24] crystallographic software package, which minimized the function $\Sigma w(\Delta F)^2$ were $w = 1/\sigma 2(F_o)$. Refinement of all non-hydrogen atoms anisotropic and BH hydrogen atoms (H10B was fixed at its difference map position) with the fixed displacement factor (1.2 × that of the host atom) (rest of hydrogen atoms included in calculated positions with fixed isotropic displacement factors) reduced the R value to 0.061 ($R_w = 0.071$) for 282 parameters. Neutral atomic scattering factors were those included in the program. Structure was plotted with ORTEP [25].

Supplementary material available for $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ includes hydrogen atom coordinates, full list of bond lengths and angles, thermal displacement parameters for heavy atoms and least-squares planes.

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References

[1] (a) F. Teixidor, R.W. Rudolph, J. Organomet. Chem. 241 (1983) 301. (b) C. Viñas, W.M. Butler, F. Teixidor, R.W. Rudolph, Organometallics 3 (1984) 503. (c) C. Viñas, W.M. Butler, F. Teixidor, R.W. Rudolph, Inorg. Chem. 25 (1986) 4369. (d) F. Teixidor, A.M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas, E. Sánchez, J. Chem. Soc. Dalton Trans. 2 (1990) 525. (e) F. Teixidor, C. Viñas, J. Rius, C. Miravitlles, J. Casabó, J. Inorg. Chem. 29 (1990) 149.

[2] F. Teixidor, J. Casabó, C. Viñas, E. Sánchez, Ll. Escriche, R. Kivekäss, Inorg. Chem. 30 (1991) 3053.

[3] F. Teixidor, C. Viñas, M.M. Abad, R. Núñez, R. Kivekäs, R. Sillanpää, J. Organomet. Chem. 506 (1995) 193.

[4] (a) L.I. Zakharkin, G.G. Zhigareva, Izv. Akad. Nauk. SSSR Ser. Khim. 5 (1965) 932. (b) H.D. Smith Jr., J. Am. Chem. Soc. 87 (1965) 1817.

[5] W.E. Hill, W. Levason, C.A. McAuliffe, Inorg. Chem. 13 (1974) 244.

[6] (a) S. AlBaker, W.E. Hill, C.A. McAuliffe, J. Chem. Soc. Dalton Trans. (1987) 1387. (b) O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, J. Chem. Soc. Dalton Trans. (1992) 1601.

[7] W.E. Hill, B.G. Rackley, L.M. Silva-Trivino, Inorg. Chim. Acta 75 (1983) 51.

[8] J.G. Contreras, L.M. Silva-Trivino, M.E. Solís, Inorg. Chim. Acta 114 (1986) 51.

[9] L.I. Zakharkin, A.V. Kazantsev, M.G. Meiramov, Zh. Obshch. Khim. 57 (1984) 1536.

[10] L.I. Zakharkin, A.V. Kazantsev, M.G. Meiramov, Izv. Akad. Nauk SSSR Ser. Khim. 7 (1984) 1641.

[11] R. Holm, F. Röhrscheid, J. Organomet. Chem. 4 (1965) 335.

[12] (a) F. Teixidor, C. Viñas, M.M. Abad, M. López, J. Casabó, Organometallics 12 (1993) 3766. (b) F. Teixidor, C. Viñas, M.M. Abad, R. Kivekäs, R. Sillanpää, J. Organomet. Chem. 509 (1996) 139. (c) R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas, M.M. Abad, Acta Chim. Scand. 50 (1996) 499. (d) F. Teixidor, C. Viñas, M.M. Abad, C. Whitaker, J. Rius, Organometallics 15 (1996) 3154.

[13] (a) F. Teixidor, A.M. Romerosa, C. Viñas, J. Rius, C. Miravitlles, J. Casabó, J. Chem. Soc. Chem. Commun. (1991) 192. (b) F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, J. Casabó, J. Chem. Soc. Chem. Commun. (1992) 1281.

[14] (a) S. Ganguly, E.M. Georgiev, J.T. Mague and D.M. Roundhill, Acta Cryst. Sect. C 49 (1993) 1169. (b) E. Lindner, J. Dettinger, H.A. Mayer, H. Kuhbauch, R. Fawzi, M. Steimann, Chem. Ber. 126 (1993) 1317.

[15] (a) F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, Organometallics 13 (1994) 2751. (b) C. Viñas, R. Núñez, M.A. Flores, F. Teixidor, R. Kivekäs, R. Sillanpää, Organometallics 14 (1995) 3952. (c) C. Viñas, R. Núñez, F. Teixidor, R. Kivekäs, R. Sillanpää, Organometallics 15 (1996) 38550.

[16] S. Liu, J. Chen, S. Peng, Y. Hsiao, M. Cheng, Inorg. Chem. 29 (1990) 1169.
[17] D.E. Berry, K.A. Beveridge, G.W. Bushnell, K.R. Dixon, Can. J. Chem. 63 (1985) 2949.
[18] C. Viñas, J. Pedrajas, J. Bertran, F. Teixidor, R. Kivekäs, R. Sillanpää, Inorg. Chem. 36 (1997) 2482.
[19] F. Teixidor, C. Viñas, M.M. Abad, R. Núñez, R. Kivekäs, R. Sillanpää, in preparation.
[20] J.R. Blackburn, R. Nordberg, F. Stevie, R.G. Albridge, M.M. Jones, Inorg. Chem. 9 (1970) 2374.
[21] J.M. Jenkins, J.G. Verkade, Inorg. Chem. 6 (1967) 1967.
[22] R.A. Walton, Spectrochim. Acta 21 (1965) 1795.
[23] C.J. Gilmore, J. Appl. Crystallogr. 17 (1982) 42.
[24] TEXSAN-TEXRAY: Single Crystal Structure Analysis Package, Version 5.0, Molecular Structure Corporation, The Woodlands, TX, 1989.
[25] C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.