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Synthesis and crystal structure of four Pd(II) complexes containing *nido* or *closo* carborane diphosphine ligands

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Abstract

Three Pd(II) complexes $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot 0.25CH_2Cl_2$ (**1**), $[Pd\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot 4CHCl_3$ (**2**) and $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**3**) have been synthesized by the reactions of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with $PdCl_2$ in acetonitrile, cyanophenyl and dichloromethane, respectively. A fourth complex, $[PdI_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**4**), was obtained by a ligand exchange reaction through the substitution of the Cl^- of complex **3** with I^-. All four complexes have been characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopy and X-ray structure determination. Single crystal X-ray determination showed that the carborane cage, *nido* for **1**, **2** and *closo* for **3**, **4**, was coordinated bidentately to the Pd atom through the two P atoms, and the geometry at the Pd atom was square-planar in all the complexes.

Keywords: Synthesis and crystal structure; Pd(II) complexes; $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$; $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$

1. Introduction

Bidentate ligands have played an important role in the development of catalytic applications of metal organic complexes [1]. Two of the fundamentals for these catalysts are that two *cis*positions of the metal center are available to perform the reaction, and bidentate phosphines have already been demonstrated to be very convenient for this sort of catalysis [2]. The influence of substitution at the cluster carbon atoms in *o*-carborane by electron rich element phosphorus has been of interest to us. Among of the derivatives of *o*-carborane, the *closo* diphosphine $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and the *nido* $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion degraded from the *closo* species are two typical bidentate phosphine ligands [3,4]. Because the two phosphorus atoms bonded to the two adjacent carbon atoms of the *o*-carborane are fixed by the geometry of the carborane skeleton in an eclipsed conformation at *cis* positions, a stable complex can be formed through a five-membered chelating ring between the ligand and a metal atom. Several Pd(II) complexes with *closo* or *nido* carborane diphosphine ligands, such as $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ [5], $[PdClMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ [6], $[PdBr_{1.133}Cl_{0.867}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$, $[PdBr_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ and $[PdBrCl_{0.541}Me_{0.459}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CHCl_3$ [7], where the structures have been characterized by X-ray diffraction, have been reported. Considering the importance of Pd as a metal in catalysis, we are also interested in this kind of complex and reported a Pd(II) complex with the formula $[PdCl(PPh_3)\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}]\cdot 1.25CH_2Cl_2$ [8]. Recently, we investigated the reactions of the *closo* diphosphine ligand with $PdCl_2$ in three different solvents and obtained three Pd(II) complexes with the formula $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot 0.25CH_2Cl_2$ (**1**), $[Pd\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot 4CHCl_3$ (**2**) and $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**3**). By using a ligand exchange reaction, we have also obtained the complex $[PdI_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**4**). All the complexes were characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopy and X-ray structure determination.

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2. Experimental

2.1. Reagents and techniques

All the reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen. Some subsequent manipulations were performed in the air. Solvents were dried with suitable drying agents, distilled under dinitrogen and deoxygenated prior to use. 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ was prepared according to the literature procedure [3]. All chemicals were purchased and used as received. Infrared spectra were recorded in the range 400–4000 cm^{-1} from KBr pellets on a Nicolet-460 FT-IR spectrophotometer. Elemental analysis (C, H) was carried out with a Perkin–Elemer 2400 II elemental analyzer. The ^1H and ^{13}C NMR were recorded on a Varian Mercury 400 spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard at 400.15 and 100.63 MHz, respectively. The ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in parts per million with respect to the references and are stated relative to external TMS for ^1H and ^{13}C NMR.

2.2. Synthetic procedures

2.2.1. Preparation of $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot 0.25CH_2Cl_2$ (**1**)

$PdCl_2$ (18.8 mg, 0.10 mmol) and 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) were added to 10 ml acetonitrile and the mixture was refluxed for 6 h under the protection of dry N_2. The yellow solid that formed was filtered off, washed with acetonitrile, and dried in vacuum (26.4 mg, 41.0%). M.p. 278–279 °C. A crystal suitable for X-ray diffraction was obtained from a dichloromethane–*n*-hexane solution. FT-IR ν_{KBr} (cm^{-1}): 3052 m, 2540 m, 1435 m, 1098 m, 741 m. ^1H NMR (400.15 MHz, $CDCl_3$): −2.1 ppm (2H, B–H–B); ^{13}C NMR (100.63 MHz, $CDCl_3$): 124–131 ppm (48C), 76.5 ppm (4C). *Anal.* Calc. for $C_{52.25}H_{60.5}B_{18}Cl_{2.50}P_4Pd_2$: C, 47.96; H, 4.66; Found: C, 47.82; H, 4.71%.

2.2.2. Preparation of $[Pd\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot 4CHCl_3$ (**2**)

$PdCl_2$ (18.8 mg, 0.10 mmol) was added to a solution of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (102.4 mg, 0.20 mmol) in 10 ml cyanophenyl and stirred for 10 h under the protection of dry N_2. The yellow solid that formed was filtered off, and dried in vacuum (42.7 mg, 38.5%). M.p. 236–237 °C. A crystal for X-ray diffraction was grown from a chloroform solution layered with ether. FT-IR ν_{KBr} (cm^{-1}): 3042 m, 2560 m, 1423 m, 1108 m, 735 m. ^1H NMR (400.15 MHz, $CDCl_3$): −2.13 ppm (2H, B–H–B); ^{13}C NMR (100.63 MHz, $CDCl_3$): 125–132 ppm (48C), 77.1 ppm (4C). *Anal.* Calc. for $C_{56}H_{64}B_{18}Cl_{12}P_4Pd$: C, 42.37; H, 4.06; Found: C, 42.30; H, 4.00%.

2.2.3. Preparation of $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**3**)

$PdCl_2$ (18.8 mg, 0.10 mmol) was added to a solution of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) in 10 ml dichloromethane. The mixture was refluxed for 3 h under the protection of dry N_2, and concentrated to 5 ml, and then 20ml *n*-hexane was added to precipitate the solid. Yield: 53.8 mg, 78.0%. M.p. 291–292 °C. A crystal suitable for X-ray diffraction was obtained from a CH_2Cl_2 solution after partial evaporation the solvent. FT-IR ν_{KBr} (cm^{-1}): 3000 m, 2600 m, 1433 m, 1080 m, 755 m. ^1H NMR (400.15 MHz, $CDCl_3$): 7.2–7.6 ppm (20H); ^{13}C NMR (100.63 MHz, $CDCl_3$): 124–132 ppm (24C), 76.3 ppm (2C). *Anal.* Calc. for $C_{26}H_{30}B_{10}Cl_2P_2Pd$: C, 45.26; H, 4.38; Found: C, 45.40; H, 4.32%.

2.2.4. Preparation of $[PdI_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**4**)

KI (1.0 mmol, 166 mg) was added to the dichloromethane solution obtained from the preparation of complex **3**. The suspension was refluxed for 5 h under the protection of dry N_2, and then filtered. The yellow filtrate was concentrated to 5 ml, and 20 ml *n*-hexane was added to precipitate the solid. Yield 43.2 mg, 49.5%. M.p. 261–262 °C. A crystal suitable for X-ray diffraction was obtained from a dichloromethane–*n*-hexane solution. FT-IR ν_{KBr} (cm^{-1}): 3030 m, 2590 m, 1445 m, 1090 m, 727 m. ^1H NMR (400.15 MHz, $CDCl_3$): 7.2–7.6 ppm (20H); ^{13}C NMR (100.63 MHz, $CDCl_3$): 125–133 ppm (24C), 77.3 ppm (2C). *Anal.* Calc. for $C_{26}H_{30}B_{10}I_2P_2Pd$: C, 35.78; H, 3.47; Found: C, 35.60; H, 3.38%.

2.3. X-ray crystallography data collection and processing

The collection of crystallographic data for the four complexes was carried out on a Bruker Smart-1000 CCD diffractometer, using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package [9]. The solvent CH_2Cl_2 in complex **1** was disordered and partially occupied atoms were refined with isotropic displacement parameters, whilst the remaining non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. All the H atoms were located in a difference Fourier map and thereafter refined isotropically, except the bridge H atoms of the *nido* carborane skeleton. These bridge H atoms were refined isotropically with fixed U values. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

3. Results and discussion

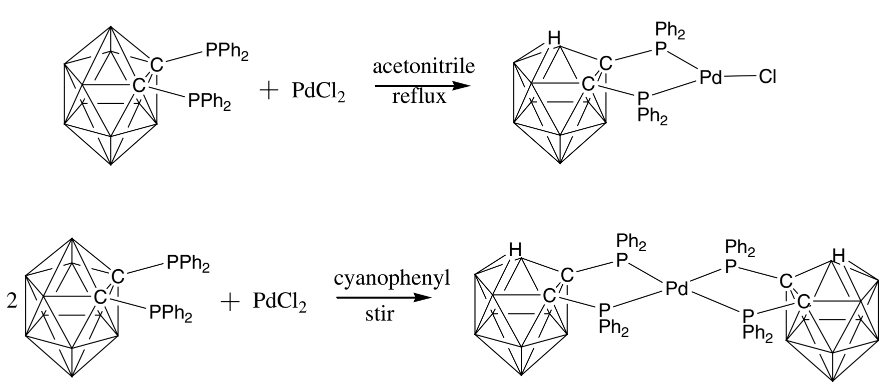
3.1. Synthesis

The metal driven degradation of the *closo* carborane diphosphine 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with C–P retention

Table 1
Details of the crystal parameters, data collection and refinement for complexes **1**, **2**, **3** and **4**

Crystal data	**1**	**2**	**3**	**4**
Empirical formula	$C_{52.25}H_{60.5}B_{18}Cl_{2.50}P_4Pd_2$	$C_{56}H_{64}B_{18}Cl_{12}P_4Pd$	$C_{26}H_{30}B_{10}Cl_2P_2Pd$	$C_{26}H_{30}B_{10}I_2P_2Pd$
Formula weight	1308.39	1587.33	689.84	872.74
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)/*n*
a (Å)	28.384(12)	22.321(9)	8.4846(15)	12.003(3)
b (Å)	16.575(7)	16.465(6)	11.0660(19)	18.202(4)
c (Å)	21.392(9)	19.922(8)	17.148(3)	14.631(3)
α (°)	90	90	89.031(2)	90
β (°)	128.635(5)	94.096(7)	85.447(2)	95.759(4)
γ (°)	90	90	75.456(2)	90
V (Å^3)	7862(6)	7303(5)	1553.5(5)	3180.4
Z	4	4	2	4
Absorption coefficient (mm^{-1})	0.652	0.818	0.891	2.644
D (Mg m^{-3})	1.105	1.444	1.475	1.823
F(000)	2634	3200	692	1672
Crystal size (mm)	0.39 × 0.38 × 0.34	0.35 × 0.33 × 0.31	0.48 × 0.33 × 0.21	0.33 × 0.31 × 0.29
Theta range (°)	2.29–25.01	1.81–25.01	1.90–25.01	2.09–25.01
Limiting indices	$-31 \leqslant h \leqslant 33$	$-26 \leqslant h \leqslant 24$	$-7 \leqslant h \leqslant 10$	$-14 \leqslant h \leqslant 13$
	$-19 \leqslant k \leqslant 19$	$-16 \leqslant k \leqslant 19$	$-13 \leqslant k \leqslant 12$	$-21 \leqslant k \leqslant 17$
	$-25 \leqslant l \leqslant 19$	$-22 \leqslant l \leqslant 23$	$-19 \leqslant l \leqslant 20$	$-12 \leqslant l \leqslant 17$
Independent reflection	6643	12664	5400	5558
Max. and min. transmission	0.8088 and 0.7851	0.7855 and 0.7627	0.8350 and 0.6744	0.5144 and 0.4757
Goodness-of-fit on F^2	1.006	1.017	1.005	1.000
$R[I > 2\sigma(I)]$	$R_1 = 0.0707$	$R_1 = 0.0707$	$R_1 = 0.0362$	$R_1 = 0.0416$
	$wR_2 = 0.1591$	$wR_2 = 0.1726$	$wR_2 = 0.0861$	$wR_2 = 0.1186$
R (all data)	$R_1 = 0.2072$	$R_1 = 0.1543$	$R_1 = 0.0529$	$R_1 = 0.0500$
	$wR_2 = 0.2128$	$wR_2 = 0.2372$	$wR_2 = 0.0978$	$wR_2 = 0.1265$
Largest difference in peak and hole (×10^2 e Å^{-3})	1.125 and −0.609	1.106 and −0.850	0.545 and −0.311	1.162 and −1.320

was first disclosed by Teixidor's group in 1993 [4]. Based on the result, much research work has been done relevant to this area by this group [10–13], and many complexes containing the *nido*-[7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$]$^-$ anion, such as Ru [14], Rh [15], Au [16,17], Ag [18] and Ni, Pd and Pt [8], have been reported. By treatment of $PdCl_2$ with the *closo* diphosphine ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ in a molar ratio 1:1 in acetonitrile under refluxing conditions, we obtained a binuclear Pd complex with the formula [Pd_2-(μ-Cl)$_2${7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$}$_2$] · 0.25CH_2Cl_2 (**1**), in which the *closo* structure of the carborane skeleton was also degraded. When the $PdCl_2$:carborane diphosphine ligand ratio was changed to 1:2 with the conditions otherwise the same, the same product was obtained, indicating that the ratio of the reactants has no influence on the result of this reaction. However, when the reaction was carried out with the starting material $PdCl_2$ and 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with a molar ratio 1:2 in cyanophenyl, the complex [Pd{7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$}$_2$] · 4$CHCl_3$ (**2**) was obtained, in which the two Cl ions of the initial $PdCl_2$ were substituted by the *nido* carborane diphosphine anion [7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$]$^-$. The reactions are shown in Scheme 1. From these results, it seemed that the solvent could play an important role in the formation process of the complexes.



Scheme 1. The reactions for the preparation of complexes **1** and **2**.

In strong nucleophilic solvents, such as ethanol [8], acetonitrile and cyanophenyl, the *closo* carborane skeleton could be degraded in the reactions of Pd compounds with the *closo* ligand. However, in mild nucleophilic solvents, for example dichloromethane, the *closo* structure of the carborane could be preserved [6,7]. The complex $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})] \cdot CH_2Cl_2$ could be obtained by the reactions of the *closo* ligand with $[PdCl_2(cod)]$ in CH_2Cl_2 or $[PdCl_2(PhCN)_2]$ in toluene [5]. Here, we revised the method for the preparation of this complex. By using $PdCl_2$ as the initial material to react with the *closo* ligand in dichloromethane under refluxing conditions, we also obtained this complex. This result further confirmed the conclusion that a mild nucleophilic solvent could avoid the degradation of the *closo* diphosphine ligand. The corresponding PdI_2 complex $[PdI_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ (**4**) was obtained through the substitution of Cl^- in $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ with I^- under refluxing conditions in CH_2Cl_2 after several hours. The bromide derivative could also be afforded by this type of ligand exchange reaction, although the process was more difficult than that for the preparation of complex **4** (refluxing for 8 days) [7].

3.2. Spectral characterization

All the complexes were characterized by FT-IR, ^1H and ^{13}C NMR spectroscopy. The IR spectra of these complexes were very similar to each other and exhibited absorptions characteristic of terminal B–H vibrations at about 2540–2600 cm^{-1}in the four complexes, which are in the normal range for B–H vibrations of 2625–2450 cm^{-1} [19]. The absorptions at 3052, 3042, 3000 and 3030 cm^{-1} might be attributed to the $v_{C–H}$ stretching vibration of the benzene rings. Several peaks were found from 1695 to 1410 cm^{-1}, which might be assigned to $v_{C=C}$ stretching vibrations. The peak at ca. 1400 cm^{-1} was the in-plane deformation mode of the benzene ring, and the peak at ca. 1100 cm^{-1} was the absorption of $v_{C(phenyl)–P}$, which was a little shifted in keeping with phosphorus coordination to the carborane moiety. The absorption at approximately 740 cm^{-1} showed the existence of cage deformation. The ^1H NMR spectra (400.15 MHz) of these complexes displayed a complex pattern of resonances at about 7.1–7.6 ppm which could be attributed to the phenyl-H of the PPh_2 groups. A resonance at ca. −2.1 ppm is the bridge H atom of B–H–B [4]. In the ^{13}C NMR spectra (100.63 MHz), a resonance at ca. $\delta = 130$ ppm could be assigned to the benzene ring C atoms, and a resonance at ca. $\delta = 77$ could be assigned to the carbon atom of carborane cage (Cc) [20].

3.3. Crystallographic data of the complexes

Crystal structures of the four complexes are shown in Figs. 1–4, respectively. Selected bond lengths and angles are given in Table 2. Complex **1** crystallizes in the monoclinic space group $C2/c$, containing four formula units in

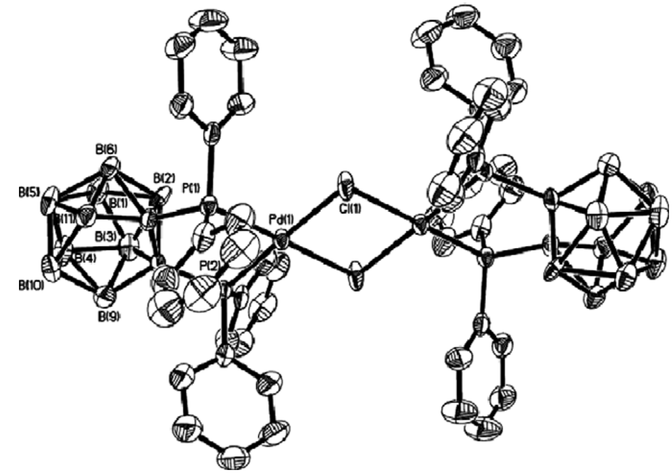


Fig. 1. Perspective view of complex unit of **1**. The H atoms are omitted for clarity.

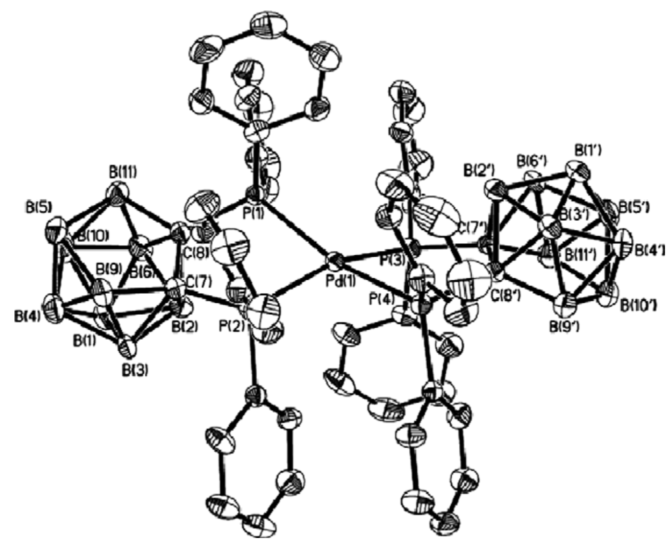


Fig. 2. Perspective view of complex unit of **2**. The H atoms are omitted for clarity.

the unit cell and the disordered solvent CH_2Cl_2. The molecular structure of complex**1** is symmetrical and the symmetry transformations used to generate equivalent atoms are $-x+1/2$, $-y+3/2$, $-z+2$. Two Cl atoms bridge the two same $Pd[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ units. The dihedral angel between central plane formed by the $[Pd_2Cl_2]$ unit and the side P(1)Pd(1)P(2) plane is only 3.3°, indicating that these two planes are almost parallel to each other. The Pd–Cl distance, 2.394(3) Å, is almost equal to the bond length of 2.405(5) Å in $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ [12], but slightly longer than the average distance of 2.338(2) Å in $[PdCl(PPh_3)\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}] \cdot 1.25\ CH_2Cl_2$ [8]. The two Pd–P bonds (2.233(2) and 2.236(2) Å) and the P–Pd–P angle (85.23(8)°) are all consistent with the average values 2.238 Å and 87.0(1)° in $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$. The average distances of P–Cc, 1.817 Å, and

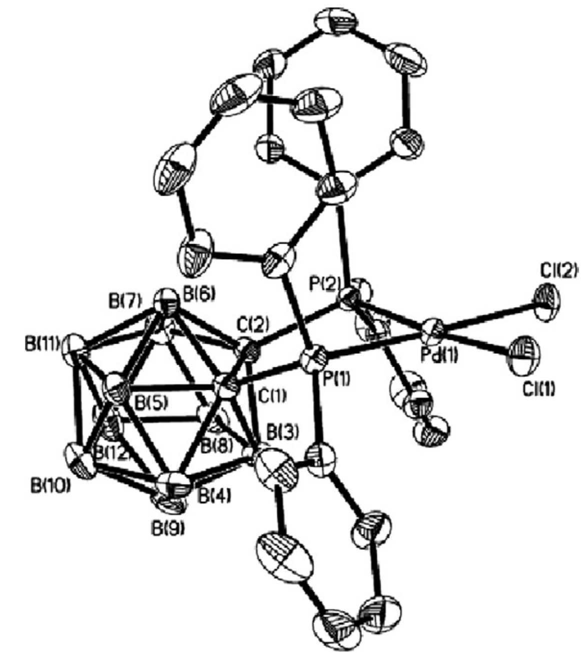


Fig. 3. The crystal structure of complex **3**. The H atoms are omitted for clarity.

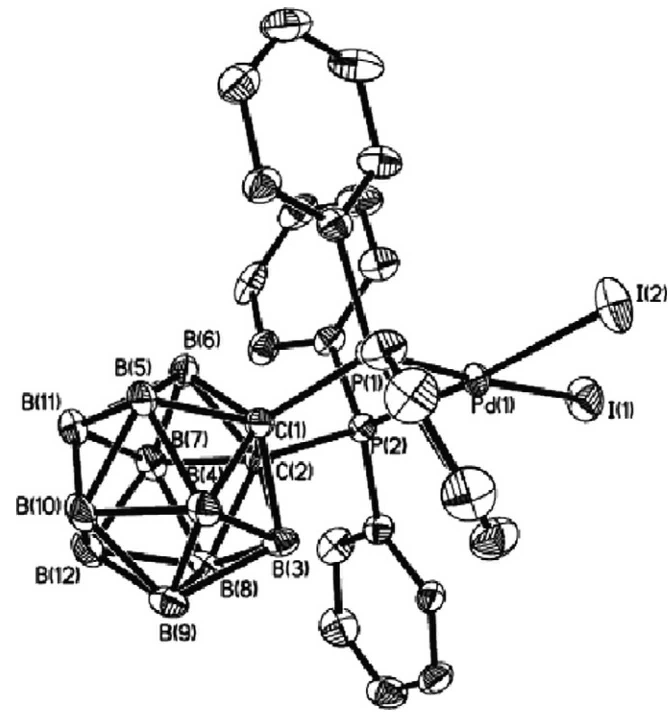


Fig. 4. The crystal structure of complex **4**. The H atoms are omitted for clarity.

Cc–Cc, 1.556(13) Å, are slightly shorter than the corresponding distances, 1.87 and 1.61(2) Å, in $[NMe_4]$-$[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}] \cdot CH_3CH_2OH$ [10], implying that coordination of the ligand to the Pd atom has an influence on these bond lengths.

Complex **2** also contains four formula units in the unit cell and the solvent $CHCl_3$, and crystallizes in the monoclinic space group $P2(1)/c$. The central Pd atom is coordinated to four P atoms coming from two *nido* carborane diphosphine anions $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. The geometry at the Pd atom is seriously distorted square-planar with a mean deviation from the P(1)P(2)P(3)P(4)Pd(1) plane of 0.3141 Å, and the angles around Pd (Table 2) deviate much from the values for a regular square-planar coordination mode. The distances of the four Pd–P bonds are almost equal to each other, and the average value of 2.362 Å is obviously longer than those in complex **1**, which can be attributed to the steric effect of the two ligands. The angles of P(1)–Pd(1)–P(2), 82.63(7)°, and P(3)–Pd(1)–P(4), 82.86(7)°, are slightly smaller than the value of 85.23(8)° in $[Pd_2(\mu\text{-}Cl)_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$. As for the other parameters in complex **2**, such as the distances of P–Cc and Cc–Cc as listed in Table 2, no noticeable differences have been found on comparison to those in complex **1**.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, **3** and **4**

1		**2**					**3** (X=Cl)	**4** (X=I)
Pd(1)–P(1)	2.233(2)	Pd(1)–P(1)	2.359(2)		Pd(1)–P(1)		2.239(1)	2.262(14)
Pd(1)–P(2)	2.236(2)	Pd(1)–P(2)	2.362(2)		Pd(1)–P(2)		2.239(1)	2.262(14)
Pd(1)–Cl(1)	2.394(3)	Pd(1)–P(3)	2.359(2)		Pd(1)–X(1)		2.333(1)	2.622(7)
Pd(1)–Cl(1)#1	2.395(2)	Pd(1)–P(4)	2.368(2)		Pd(1)–X(2)		2.330(1)	2.614(7)
P(1)–C(7)	1.814(9)	P(1)–C(7)	1.824(8)		P(1)–C(1)		1.873(4)	1.883(5)
P(2)–C(8)	1.819(9)	P(2)–C(8)	1.833(8)		P(2)–C(2)		1.883(3)	1.885(5)
C(7)–C(8)	1.556(13)	P(3)–C(7′)	1.817(8)		C(1)–C(2)		1.677(5)	1.687(7)
P(1)–Pd(1)–P(2)	85.23(8)	P(4)–C(8′)	1.832(8)		P(2)–Pd(1)–P(1)		89.73(4)	91.37(5)
P(1)–Pd(1)–Cl(1)	94.16(8)	C(7)–C(8)	1.556(11)		P(2)–Pd(1)–X(2)		174.09(4)	175.39(4)
Cl(1)–Pd(1)–Cl(1)#1	85.18(8)	P(1)–Pd(1)–P(4)	160.55(7)		P(1)–Pd(1)–X(2)		88.44(4)	87.77(4)
P(2)–Pd(1)–Cl(1)#1	95.33(8)	P(1)–Pd(1)–P(3)	103.93(7)		P(2)–Pd(1)–X(1)		89.77(4)	88.88(4)
P(2)–Pd(1)–Cl(1)	177.3(11)	P(1)–Pd(1)–P(2)	82.63(7)		P(1)–Pd(1)–X(1)		178.75(4)	176.97(4)
P(1)–Pd(1)–Cl(1)#1	177.8(11)	P(3)–Pd(1)–P(4)	82.86(7)		X(2)–Pd(1)–X(1)		91.94(4)	91.74(2)
C(7)–P(1)–Pd(1)	111.3(3)	P(2)–Pd(1)–P(4)	96.99(7)		C(1)–P(1)–Pd(1)		108.0(10)	108.1(2)
C(8)–P(2)–Pd(1)	110.9(3)	P(3)–Pd(1)–P(2)	160.52(7)		C(2)–P(2)–Pd(1)		108.1(11)	107.6(2)
C(7)–C(8)–P(2)	114.2(6)	C(7)–C(8)–P(2)	116.2(5)		C(2)–C(1)–P(1)		113.1(2)	113.8(3)
C(8)–C(7)–P(1)	113.5(5)	C(8)–C(7)–P(1)	114.2(5)		C(1)–C(2)–P(2)		113.3(2)	114.8(3)

Symmetry transformations used to generate equivalent atoms for complex **1**: $-x + 1/2$, $-y + 3/2$, $-z + 2$.

As for complex **4**, the Pd atom is also four coordinate, in which two positions are occupied by the *closo* carborane diphosphine 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$, and the other two come from two I atoms in *cis* positions, fulfilling the slightly distorted square-planar coordination. The mean derivation from the P(1)P(2)Pd(1)I(1)I(2) plane is only 0.0258 Å. The two I–Pd bond lengths are 2.622(7) and 2.614(7) Å, which are comparable to the analogous distances of 2.6649(8) and 2.6446(10) Å in $[PdI_2(dppe)]$ [21]. The I–Pd–I angle of 91.74(2)° is almost equal to Cl–Pd–Cl angle of 91.94(4)° in complex **3**. Other bond lengths and angles in the coordination sphere of $[PdI_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ agree well with the corresponding values in $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})] \cdot CH_2Cl_2$ [5]. Comparison of the configuration of the *closo* carborane diphosphine ligand in complex **4** with that in the free 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ ligand reveals differences. In the free ligand the P(1)–C(1)–C(2)–P(2) torsion angle is 10.6(3)° [22], while this angle in complex **4** is only 0.6(5)°. This data indicates that coordination of the ligand to Pd(II) alters the symmetry of the ligand. On comparison to that in the free *closo* ligand, the symmetry of the ligand in the complex **4** closely approaches C_{2v}.

4. Conclusions

In this paper we have reported four Pd(II) complexes containing *closo* or *nido* carborane diphosphine ligands, which were obtained by the reactions of the *closo* ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with $PdCl_2$ in different solvents or by a ligand exchange reaction. The results indicate that the solvent plays an important role in these reactions, both for the degradation of the *closo* carborane skeleton and for the formation process of the complexes.

5. Supplementary material

CCDC 608198, 608199, 608201, 608200, contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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