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Palladium-mediated substitution of the *closo*-$B_{12}H_{12}(-2)$ and *nido*-7,8-$C_2B_9H_{12}(-1)$ ions by PMe_2Ph: The single-crystal structure studies of 1,7-$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$ and 9-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$

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Abstract

Treatment of Na_2[*closo*-$B_{12}H_{12}$] with one mole equivalent of $(PMe_2Ph)_2PdCl_2$ in THF at room temperature formed Na[*closo*-(PMe_2Ph)-$B_{12}H_{11}$], 1,7- and 1,12-$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$ in moderate yield. Reaction of K[*nido*-7,8-$C_2B_9H_{12}$] with one half a mole equivalent of $(PMe_2Ph)_2PdCl_2$ in CH_2Cl_2 at room temperature formed a mixture of 9-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ and 10-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ in overall good yield. Single-crystal X-ray structures of 1,7-$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$ and 9-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ are reported.

Keywords: Phosphine-substituted carborane; Palladium-mediated substitution; Polyhedral borane; Boron

1. Introduction

The use of palladium(II) reagents in synthetic organic chemistry is widespread, and a large variety of transformations may be accomplished [1]. The Suzuki reaction, the palladium catalyzed coupling of an organoboron reagent with aryl- or alkenylhalides, is a very powerful method for carbon–carbon bond formation [2].

The B-alkyl Suzuki–Miyaura cross-coupling reaction extends this process to involve an sp^3 carbon in the coupling event [3]. The B-arylation of *p*-carborane was accomplished by palladium-catalyzed cross-coupling of an arylboronic acid and 2-I-*p*-carborane [4]. Palladium-catalyzed borane–olefin or carborane–olefin coupling reactions were reported by Sneddon and coworkers [5]. In these cases, a B–H bond must be "activated" so that substitution may take place.

This type of reaction suggests the possibility that easily-accessible palladium(II) coordination compounds may be used to activate a B–H bond of a polyhedral borane or heteroatom borane and substitute a ligand there, as represented in the general case of:

$$L_2PdCl_2 + [(cage)B-H]^{n-} \rightarrow [(cage)B-L]^{(n-1)-} \text{“}L_nPdX_m\text{”} \quad (1)$$

In this type of reaction, a neutral 2-electron donor ligand (:L) transfers from palladium to a polyhedral borane anion site, substituting for a hydride ion resulting in a "charge-compensated" borane species. There are also as yet uncharacterized palladium byproduct(s) represented by "L_nPdX_m" species in Eq. (1).

Numerous charge-compensated polyhedral boranes and carboranes were described over 40 years ago [6,7]. These included phosphine-substituted $B_{12}H_{12}(-2)$ derivatives [6]. Reaction of PMe_3 with diborane-6 in a stainless steel vessel at 175 °C for 10 h formed $[H_2B(PMe_3)_2][PMe_3$-$B_{12}H_{11}]$ and

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a small amount of $(PMe_3)_2B_{12}H_{10}$ [6]. These compounds were characterized by elemental analysis only. The possibility of isomers of $(PMe_3)_2B_{12}H_{10}$ was not addressed.

During our studies of the syntheses of pallada-diarsaboranes, we obtained some products having charge-compensating Lewis base ligands bonded to cage boron atoms [8]. Many other transition metal-mediated substitution reactions of phosphines (PR_3) onto boron atoms of polyhedral cage molecules have been reported. For example, reaction of $PdI_2(PPh_3)_2$ with $Cs[TeB_{10}H_{11}]$ in refluxing toluene formed 2-I-2-PPh_3-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$ in good yield [9]. Another example is the conversion of 8,8-$(PMe_2Ph)_2$-*nido*-8,7-$PtCB_9H_{11}$ in refluxing toluene to 6-PMe_2Ph-*closo*-1-CB_9H_8 in good yield [10]. These results lead us to study more generally some palladium-assisted substitution reactions of $B_{10}H_{10}(-2)$ and $B_{12}H_{12}(-2)$ ions, including a brief mention of 1,7-$(PMe_2Ph)_2B_{12}H_{10}$ [11]. Recently, the synthesis and crystal structure determination of $N(n\text{-}Bu)_4[PPh_3\text{-}B_{12}H_{11}]$ was reported [12]. This derivative was prepared by reaction of $[N(n\text{-}Bu)_4]_2[B_{12}H_{11}I]$ with $Pd(Ph_3)_4$.

In this report, we describe in detail the reaction of $(PMe_2Ph)_2PdCl_2$ with $Na_2[B_{12}H_{12}]$ and also with K[7,8-$C_2B_9H_{12}$] to give several charge-compensated products in moderate yields.

2. Experimental

2.1. Physical measurements

Boron (^{11}B) NMR spectra were obtained at 115.85 MHz (21 °C) with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3(OEt_2)$. Phosphorus (^{31}P) NMR spectra were obtained at 146.2 MHz (21 °C) and externally referenced to 85% H_3PO_4. Proton (^1H) NMR spectra were obtained at 361.1 MHz (21 °C) and internally referenced to trace protonated solvent. In all NMR spectra, positive chemical shifts were downfield. Melting points were obtained in sealed, evacuated capillaries and are uncorrected.

2.2. Materials

All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5. Potassium dodecahydro-7,8-dicarba-*nido*-undecaborate(1−), K[7,8-$C_2B_9H_{12}$], was prepared by a literature method [13]. Bis(dimethylphenylphosphine) palladium(II) chloride was prepared by the method of Wild et al. [14].

2.3. $(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$ isomers and $Na[(PMe_2Ph)$-*closo*-$B_{12}H_{11}]$

In a typical reaction scheme, $Na_2B_{12}H_{12}$ (1.81 g, 9.6 mmol) was placed in a 500 mL round-bottom flask equipped with a magnetic stir bar and dissolved in 40 mL dry THF. In a separate flask, $(PMe_2Ph)_2PdCl_2$ (4.35 g, 9.6 mmol) was dissolved in 240 mL of dry THF and then transferred slowly via cannula to the stirred solution of $Na_2B_{12}H_{12}$. The mixture was stirred at room temperature for 1 day during which time the color changed from orange to brown. The mixture was vacuum filtered to remove solid material. To the clear THF solution was added an excess of $NaBH_4$ to reduce all remaining palladium species to Pd^0. Vigorous gas evolution occurred as the mixture was brought to reflux, which was continued for 6 h. The mixture was left at room temperature over night to complete the reduction. The mixture was filtered through a coarse-fritted filter under nitrogen to remove the reduced metal solids (*Caution:* The filtered solids may spontaneously ignite if exposed to air). The THF was removed from the filtrate by rotary evaporation leaving a thick white oil. This crude mixture was dissolved in CH_2Cl_2 and mixed with 3 g of silica gel (Merck grade 60, 230–400 mesh, 60 Å). The CH_2Cl_2 was removed in vacuo and the solids were packed on a 35 cm × 2.4 cm silica gel chromatography column, and eluted initially with 1:1 (v/v) toluene:CH_2Cl_2. There were four bands. Band I, $R_f = 0.96$ by TLC (CH_2Cl_2 mobile phase, I_2 development) was determined by ^{11}B NMR to be $(PMe_2Ph)BH_3$, $^{11}B\{^1H\}$, −38 ppm, $J_{B-P} = 61$ Hz [15] Band II, $R_f = 0.85$ was a white solid (353 mg, 8.82% yield) and $R_f = 0.6$ was determined to be 1,12-$(PMe_2Ph)_2$-$B_{12}H_{10}$ by ^{11}B NMR (see Table 1). Band III, 1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$, a white solid, m.p. 202–206 °C (1.201 g, 30.14% yield). And band IV was eluted with 1:1 CH_2Cl_2:CH_3CN and was found to be a relatively insoluble compound, whose ^{11}B NMR spectrum was consistent with Na-[(PMe_2Ph)-$B_{12}H_{11}$] (see Table 2–6).

2.4. PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ isomers

In a two-neck, round-bottom flask equipped with a septum and nitrogen inlet were placed K[*nido*-7,8-$C_2B_9H_{12}$] (172 mg, 0.998 mmol) and $(PMe_2Ph_2PdCl_2$ (226 mg, 0.498 mmol), and 25 mL dry distilled CH_2Cl_2. The dicarbollide salt did not fully dissolve. The solution gradually darkened from yellow to orange to brown while stirring overnight. The reaction mixture was filtered on a coarse-fritted funnel, to leave behind some gray solids. The brown filtrate was rotary evaporated, and the remaining solids extracted with benzene. An excess of $NaBH_4$ was added to the benzene solution to reduce all remaining palladium species to Pd^0. The solution was brought to reflux for 4 h. The mixture was filtered through a coarse-fritted funnel to remove fluffy grayish solids, resulting in a nearly colorless filtrate. The benzene was rotary evaporated to a yellow oil (221 mg, 81.9% crude yield). ^{11}B NMR indicated that the oil consisted of a mixture of 9-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ (major product) and 10-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ (minor product). Subsequent crystallization from CH_2Cl_2/pentane at 5 °C yielded pale yellow needles of 9-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$.

Table 1
^{11}B NMR data

Compound	Chemical shift (ppm), (relative intensities) [$J_{^{11}B-H}$ (Hz)]
1,12-$(PMe_2Ph)_2$-$B_{12}H_{10}$	−13.8, (10B) [129]; −16.1, (2B) [$J_{^{11}B-^{31}P} \cong 230$ Hz]
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$	−11.9, (4B); −13.6, (4B) [159]; −15.3, (2B); −16.2, (2B) [$J_{^{11}B-^{31}P} \cong 150$ Hz]
Na[(PMe_2Ph)-$B_{12}H_{11}$]	−11.1, (1B) [132]; −13.4, (5B) [138]; −14.9, (5B) [141] −17.6, (1B) [$J_{^{11}B-^{31}P} = 141$ Hz]
N(*n*-Bu)$_4$[PPh_3-$B_{12}H_{11}$][a]	−8.4, (1B); −12.3 (5B); −13.5, (5B); −17.9 (1B) [$J_{^{11}B-^{31}P} = 134$ Hz]
9-PMe_2Ph-7,8-$C_2B_9H_{11}$	−4.1 (1B), [138]; −10.1 (1B), [145]; −15.6 (1B), [$J_{^{11}B-^{31}P} = 155$ Hz]; −16.1 (1B); −18.0 (1B); −23.6 (1B) [156]; −25.5 (1B) [145] −28.3 (1B) [129]; −36.2 (1B) [143]
10-PMe_2Ph-7,8-$C_2B_9H_{11}$	−11.0 (2B); −15.0 (1B); −16.1 (2B); −20.7 (2B) [154]; −34.5 (1B) [$J_{^{11}B-^{31}P} \cong 145$ Hz] −36.1 (1B)
9-PPh_3-7,8-$C_2B_9H_{11}$[b]	−2.97 (1B); −9.26 (1B); −14.89 (1B) [$J_{^{11}B-^{31}P} = 155$ Hz]; −16.37 (1B) −17.80 (1B); −23.46 (1B), −25.50 (1B) −26.89 (1B); −36.04 (1B)
9-PPh_3-7,8-$C_2B_9H_{11}$[c]	−1.42 (1B); −7.76 (1B); −12.98 (1B) [$J_{^{11}B-^{31}P} = 149$ Hz] −14.58 (1B); −16.20 (1B); −21.86 (1B) −23.78 (1B); −25.33 (1B); −34.47 (1B)
10-PPh_3-7,8-$C_2B_9H_{11}$[c]	−9.86 (2B); 14.16 (3B); −19.02 (2B) −32.18 (1B) [$J_{^{11}B-^{31}P} = 150$ Hz]; −35.83 (1B)
9-PPh_2Me-7,8-$C_2B_9H_{11}$[c]	−2.34 (1B); −8.56 (1B); −12.61 (1B) [$J_{^{11}B-^{31}P} = 164$ Hz] −15.12 (1B); −16.60 (1B); −22.13 (1B); −23.90 (2B); −26.52 (1B); −35.04 (1B)
10-PPh_2Me-7,8-$C_2B_9H_{11}$[c]	−9.72 (2B); −14.50 (3B); −19.25 (2B) −33.02 (1B) [$J_{^{11}B-^{31}P} = 150$ Hz]; −36.05 (1B)

[a] Ref. [12], $CHCl_3$ solvent.
[b] Ref. [22], solvent, CH_2Cl_2.
[c] Refs. [20,21].

Table 2
^{1}H NMR data

Compound	Chemical shift (ppm), (relative intensities) assignt, multiplicity, $^2J_{H-P}$ (Hz)
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$[a]	1.78, (12H), P*Me*$_2$, doublet, 12.2 7.4–7.6, (10H), P*Ph*, multiplet
1,12-$(PMe_2Ph)_2$-$B_{12}H_{10}$	1.56, (12H), P*Me*$_2$, doublet, 10.3 7.4–7.6, (10H), P*Ph*, multiplet
9-PMe_2Ph-7,8-$C_2B_9H_{11}$	1.81, (3H), PMe_2, doublet, 11.9 1.89, (3H), PMe_2, doublet, 12.1 2.23 (2H), *H*-Carb. 7.58–7.77, (5H) P*Ph*, multiplet

[a] $CDCl_3$ solvent.

Table 3
^{31}P{^{1}H} NMR data

Compound	Chemical shift (ppm), multiplicity, J_{B-P} (Hz)
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$	−8.9, 1:1:1:1 quartet, 150
9-PMe_2Ph-7,8-$C_2B_9H_{11}$	−7.8, 1:1:1:1 quartet, 151

Table 4
Crystallographic data

Compound	1,7-(PMe_2Ph)-$B_{12}H_{10}$	9-PMe_2Ph-7,8-$C_2B_9H_{11}$
Molecular weight	416.10	270.55
Crystal system, *Z*	triclinic, $P\bar{1}$, 2	monoclinic, *C*2/*c*, 8
Unit cell		
A (Å)	9.607(1)	29.978(9)
B (Å)	14.997(2)	6.769(2)
C (Å)	8.934(1)	17.063(5)
α (°)	99.32(0)	
β (°)	109.86(0)	115.02(1)
γ (°)	88.05(0)	
V (Å^3)	1194.31	3137.44
ρ_{calc} (g cm^{-3})	1.157	1.146
λ (Å)	0.71069	0.71069
μ (cm^{-1})	1.799	1.481
Det-samp distance (cm)	22.5	22.5
Samp-source distance (cm)	23.5	23.5
Takeoff angle (°)	2.0	2.0
Average ω scan width at half-height (°)	0.25	0.25
Scan speed (°/min)	4.0	10.0
Scan width (°)	2.0 + dispersion	1.8 + dispersion
Single bkgd time at extremes of scan (s)	4	4
Aperture size (mm)	3.0 × 4.0	3.0 × 4.0
Collection limit (2θ, °)	6–45	6–45
Total number of reflections	3384	2296
Number of unique intensity	3133	2059
Number with $F > 0.0$	3018	1927
Number with $F > 2.33^*\sigma(F)$	2714	1626
R for averaging	0.011	0.032
Final residuals		
R(*F*)	0.0338	0.0403
$R_w(F)$	0.0366	0.0425
Goodness-of-fit for last cycle	1.938	1.334
Maximum Δ/σ for last cycle	0.05	0.11

Det-samp dist, detector to sample distance; Samp-source distance, sample to X-ray source distance; Single bkgd time at extremes of scan, single background time at extremes of scan.

2.5. Crystal structure determinations – general

The diffractometer utilized for data collection was designed and constructed locally. The apparatus comprised a Picker X-ray generator and Picker four-circle goniostat equipped with a Furnas Monochromater (HOG crystal) was modified by addition of stepping motors (Slo-Syn) on each of the four axes, and a fifth motor drives a 20-position filter/attenuator wheel. The latter allows top/bottom-left/right alignment of reflections. All motors are driven by a locally designed ISA board in an IBM-PC compatible computer. The computer also has a timer/scaler board which is used to accumulate the counts from the scintillation counter

Table 5
Selected bond distances (Å) for 1,7-$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$

P(13)–B(1)	1.9055(25)	B(4)–B(9)	1.787(4)
P(22)–B(7)	1.9113(25)	B(5)–B(6)	1.792(4)
B(1)–B(2)	1.768(3)	B(5)–B(9)	1.776(4)
B(1)–B(3)	1.760(3)	B(5)–B(10)	1.785(4)
B(1)–B(4)	1.769(3)	B(6)–B(10)	1.788(4)
B(1)–B(5)	1.765(4)	B(6)–B(11)	1.780(4)
B(1)–B(6)	1.775(3)	B(7)–B(8)	1.770(3)
B(2)–B(3)	1.804(3)	B(7)–B(11)	1.778(3)
B(2)–B(6)	1.794(4)	B(7)–B(12)	1.772(3)
B(2)–B(7)	1.769(3)	B(8)–B(9)	1.787(4)
B(2)–B(11)	1.789(3)	B(8)–B(12)	1.799(4)
B(3)–B(4)	1.789(3)	B(9)–B(10)	1.802(4)
B(3)–B(7)	1.763(3)	B(9)–B(12)	1.787(4)
B(3)–B(8)	1.791(4)	B(10)–B(11)	1.783(4)
B(4)–B(5)	1.790(4)	B(10)–B(12)	1.790(4)
B(4)–B(8)	1.773(4)	B(11)–B(12)	1.795(4)

Table 6
Selected bond distances (Å) for 9-(PMe_2Ph)-*nido*-7,8-$C_2B_9H_{11}$

P(12)–B(9)	1.905(3)	B(3)–C(8)	1.735(4)
B(1)–B(2)	1.745(5)	B(4)–B(5)	1.762(5)
B(1)–B(3)	1.774(5)	B(4)–C(8)	1.738(4)
B(1)–B(4)	1.780(5)	B(4)–B(9)	1.761(4)
B(1)–B(5)	1.781(4)	B(5)–B(6)	1.811(5)
B(1)–B(6)	1.811(5)	B(5)–B(9)	1.752(5)
B(2)–B(3)	1.760(5)	B(5)–B(10)	1.798(5)
B(2)–B(6)	1.758(5)	B(6)–B(10)	1.800(5)
B(2)–C(7)	1.694(4)	B(6)–B(11)	1.799(5)
B(2)–B(11)	1.796(5)	C(7)–C(8)	1.534(4)
B(3)–B(4)	1.779(4)	C(7)–B(11)	1.630(5)
B(3)–C(7)	1.705(4)	C(8)–B(9)	1.589(5)
B(10)–B(11)	1.870(5)	B(9)–B(10)	1.792(5)

used with the goniostat. The control software, PCPS.EXE, is the Picker software written by W. E. Streib of the Indiana University Molecular Structure Center (IUMSC). The software for structure solution and refinement include SHELXTL-PC and other versions of SHELX, as well as the XTEL program library.

2.6. Crystal structure determination of 1,7-$(PMe_2Ph)_2B_{12}H_{10}$

A typical crystal of 1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$ was grown by slow evaporation from a 1:1 solution of toluene and CH_2Cl_2. The crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −174 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, corresponding to a triclinic space group. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, $P\bar{1}$.

All hydrogen atoms were clearly visible in a difference Fourier phased on the nonhydrogen atoms, and were refined isotropically in the final cycles of refinement. A final difference Fourier was essentially featureless, the largest peak being 0.34 e/Å^3.

2.7. Crystal structure determination of 9-(PMe_2Ph)-7,8-$C_2B_9H_{11}$

Pale yellow crystals of a 9-$PPhMe_2$-7,8-$C_2B_9H_{11}$ were grown from a solution of CH_2Cl_2/pentane held at 5 °C. A small, well-formed fragment of a larger crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −174 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to one of the centered space groups $C2/c$ or Cc. Subsequent solution and refinement confirmed the centrosymmetric choice, $C2/c$.

Data were collected using a continuous θ, 2θ scan technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MULTAN 78) and standard Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier phased on the nonhydrogen atoms, and were included in the least squares refinement.

A final difference Fourier was essentially featureless, the largest peak being 0.32 e/Å^3. It was observed that this peak was near the bridging hydride in the B_9C_2 cage, and in fact would appear to bridge the two carbon atoms. Attempts to model this as a partial occupancy bridging hydrogen (with the occupancy of the located bridge allowed to vary also) did not lead to a successful convergence. In all probability, the hydrogen may "float" on the face of the carborane, but the crystallographic evidence is lacking.

The structure is essentially the same as that reported for 9-PPh_3-*nido*-7,8-$C_2B_9H_{11}$ [22] and 9-$PMePh_2$-*nido*-7,8-$C_2B_9H_{11}$ [20,21]. The diphenylmethyl phosphine structure reported by Zakharkin et al. is remarkably similar, and is nearly isostructural [20,21].

3. Results and discussion

3.1. PMe_2Ph derivatives of the $B_{12}H_{12}^{-2}$ ion

Reaction of $Na_2[B_{12}H_{12}]$ with $(PMe_2Ph)_2PdCl_2$ at ambient temperature gave three phosphine-substituted products, each in low yield, namely $Na[(PMe_2Ph)B_{12}H_{11}]$, 1,7-$(PMe_2Ph)_2B_{12}H_{10}$ (30% yield, approx.) and 1,12-$(PMe_2Ph)_2B_{12}H_{10}$ (8% yield, approx.). The crude reaction mixture was subsequently treated with excess sodium borohydride to reduce all palladium-containing intermediates, "L_nPdX_m" to palladium metal. The first band to be eluted during column chromatography on silica gel, 1:1 (v/v) toluene:CH_2Cl_2 was $(PMe_2Ph)BH_3$ identified by ^{11}B NMR, $\delta_{^{11}B} = -38$ ppm, $J_{B-P} = 61$ Hz [15]. The boron in this compound originated from $NaBH_4$, added to the reaction mixture during workup and was not due to degradation of the $B_{12}H_{12}(-2)$ ion.

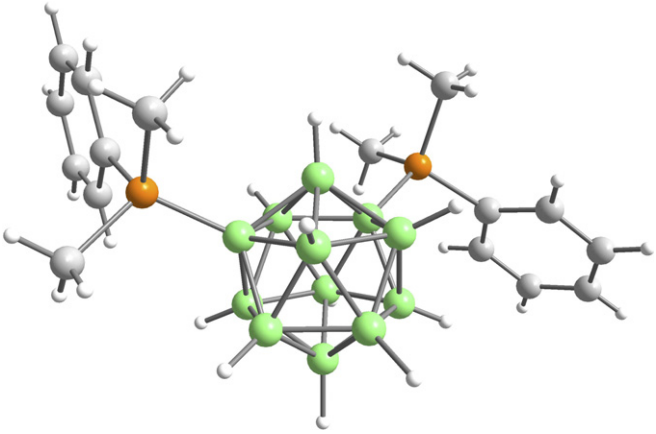

Fig. 1. X-ray structure of 1,7-$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$.

The 1,12-$(PMe_2Ph)_2B_{12}H_{10}$ isomer was identified by its ^{11}B NMR spectrum (see Table 1), which indicates a high symmetry (D_{5h}) and excludes the 1,2- or 1,7-isomer configuration for this product.

An X-ray structural determination (Fig. 1) has been undertaken on the other bis-phosphine isomer which was isolated and it conclusively proves it to be the 1,7-isomer.

The 1,7-$(PMe_2Ph)_2B_{12}H_{10}$ product was obtained in the higher yield and is statistically the most favored bis-phosphine derivative. Note that steric factors may be important in this substitution process since to-date no 1,2-bis-phosphine product has been observed.

The X-ray structure (Fig. 1) shows no anomalous distances or angles. The B–P distances, 1.9055 and 1.9113 Å are quite usual, as are the B–B distances, which all are in the range 1.760–1.804 Å. This compares favorably with the B–P distance of 1.928 Å found for $[N(n\text{-}Bu)_4][(PPh_3)\text{-}B_{12}H_{11}]$ [12].

The B–P coupling constant for the 1,7-disubstituted product as determined by ^{31}P NMR was 150 Hz. This is within the range of values observed for similar phosphine-borane compounds (118–200 Hz) [16,17]. The value could not be corroborated by ^{11}B NMR, however, because the doublet was not well-enough resolved for accurate measurement. The B–P coupling constant observed for $Na[(PMe_2Ph)\text{-}B_{12}H_{11}]$ in the ^{11}B NMR spectrum was 141 Hz. This agreed well with the B–P value reported previously for $N(n\text{-}Bu)_4\text{-}[PPh_3\text{-}B_{12}H_{11}]$ of 134 Hz [12].

3.2. PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ isomers

Reaction of *nido*-7,8-$C_2B_9H_{12}(-1)$ ion with $(PMe_2Ph)_2\text{-}PdCl_2$ at ambient temperature yielded two isomers of (PMe_2Ph)-*nido*-7,8-$C_2B_9H_{11}$. The combined crude yield of both the asymmetric 9-isomer and symmetric 10-isomer was 82%. The ^{11}B NMR spectrum of the mixture suggested that the 9-isomer predominated by approximately 2:1. Preference for reaction at the 9 position has been observed in electrophilic substitution reaction of *nido*-7,8-$C_2B_9H_{12}(-1)$ ion by I_2 [18], by $(C_5H_5)Fe(CO)_2$(alkene)(+1) ion [19] and by Ph_2PCl [20,21]. The ^{11}B NMR spectra of 9- and 10-PMe_2Ph-*nido*-7,8-$C_2B_9H_{11}$ agree with those of the two isomers of the previously-reported (PPh_3)-*nido*-7,8-$C_2B_9H_{11}$ [20–23] and $(PMePh_2)$-*nido*-7,8-$C_2B_9H_{11}$ [20,21] (see Table 1). The asymmetric 9-isomer has nine distinct resonances in its spectrum, whereas the C_s symmetric 10-isomer has six resonances in a 2:2:2:1:1:1 area ratio. In each of the 9-isomer derivatives, the resonance at approximately −12.6 to −15.6 ppm displayed $^{11}B\text{–}^{31}P$ spin–spin coupling of 149–164 Hz. For the 10-isomer derivatives, the resonance at −32.1 to −34.5 ppm displayed $^{11}B\text{–}^{31}P$ coupling of 145–150 Hz.

The X-ray structure (Fig. 2) shows no anomalous distances or angles. The B–P distance of 1.905 Å is typical of

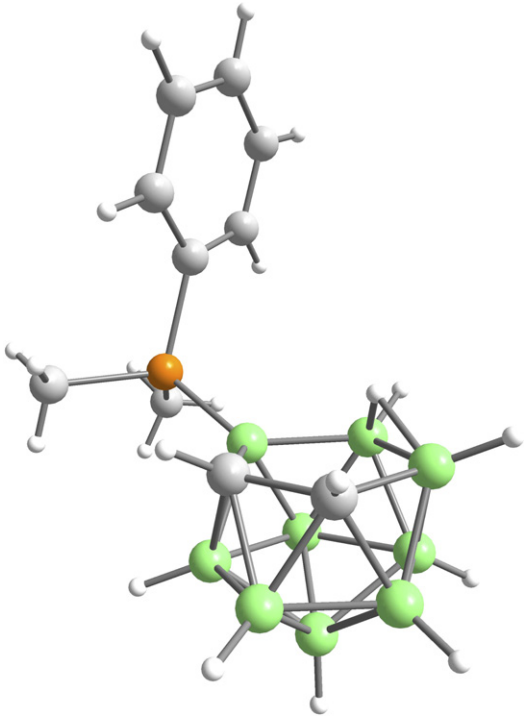

Fig. 2. X-ray structure of 9-(PMe_2Ph)-*nido*-7,8-$C_2B_9H_{11}$.

phosphine boranes; the B–B distances are all in the range 1.745–1.870 Å, and the B–C distances are slightly shorter at 1.589–1.738 Å which is typical of carborane species.

Appendix A. Supplementary material

CCDC 634413 and 634414 contain the supplementary crystallographic data for this paper. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.04.025.

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