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Synthesis and crystal structure of three *nido* 11-vertex platinaborane clusters

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The reaction of $[PtCl_2(PPh_3)_2]$ with *closo*-$B_{10}H_{10}^{2-}$ in ethanol under reflux conditions gave two *nido* 11-vertex platinaundecaborane clusters: $[(PPh_3)_2PtB_{10}H_{10}$-8,10-$(OEt)_2]\cdot CH_2Cl_2$ (1) and $[(PPh_3)_2PtB_{10}H_{11}$-11-OEt$]\cdot CH_2Cl_2$ (2). A novel $B_{10}H_{10}^{2-}$ deboronated *nido* 11-vertex diplatinaundecaborane $[(\mu$-$PPh_2)(PPh_3)_2Pt_2B_9H_6$-3,9,11-$(OEt)_3]\cdot CH_2Cl_2$ (3) was obtained when the same reaction was carried out under solvothermal conditions. All of these compounds were characterized by infrared spectroscopy, NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction. Both clusters 1 and 2 have a *nido* 11-vertex $\{PtB_{10}\}$ polyhedral skeleton in which the Pt atom lies in the open PtB_4 face. Each Pt atom connects with four B atoms and two P atoms of the PPh_3 ligands. Cluster 3 has a *nido* 11-vertex $\{Pt_2B_9\}$ polyhedral skeleton in which two Pt atoms sit in neighbouring positions of the open Pt_2B_3 face, bridged by a PPh_2 group. Each Pt atom connects three B atoms and a P atom of the PPh_3 ligand.

KEYWORDS: nido; platinaborane cluster; solvothermal synthesis; crystal structure

INTRODUCTION

In recent years, boron cluster chemistry has seen much progress and has developed into a fruitful area that includes neutral boranes and their anions, metallaboranes, carboranes and their derivatives, metallacarboranes and main group heteroboranes and their derivatives. These compounds offer potential for many useful applications, including boron neutron capture therapy (BNCT) of tumours, solvent extraction, non-linear optics, liquid crystals, ion-selective electrodes, catalysts and host–guest chemistry.[1–5] At the same time, the emergence of topological structure theory and polyhedral skeleton electron pair theory has pushed new developments in structural chemistry and expanded the research area. Thus research into the reaction and structure of boron-metal-containing clusters is very important with regard to theory and applications.

The *nido*-7-platinaundecaboranes have been investigated extensively, such as unsubstituted compounds in boron cages: $[(PR_3)_2PtB_{10}H_{12}]$ (R = Et, Bu, Me_2Ph).[6–8] Reactions of *closo*-$B_{10}H_{10}^{2-}$ with $[PtCl_2(PPh_3)_2]$ in methanol or isopropanol can also result in the 11-vertex *nido*-7-platinaundecaboranes substituted by OMe or O*i*Pr at different positions[9,10] in which the *closo*-borane dianion $B_{10}H_{10}^{2-}$ expands to a *nido* 11-vertex icosahedral fragment. When the reaction of *closo*-$B_{10}H_{10}^{2-}$ with $[PtCl_2(PPh_3)_2]$ was carried out in ethanol the 11-vertex ethoxy-substituted *nido*-7-platinaundecaboranes $[(PPh_3)_2PtB_{10}H_{11}$-8-OEt], $[(PPh_3)_2PtB_{10}H_{11}$-9-OEt][11] and $[(PPh_3)_2PtB_{10}H_{11}$-2-OEt][12] can be obtained. We also investigated the reaction of *closo*-$B_{10}H_{10}^{2-}$ with $[PtCl_2(PPh_3)_2]$ in ethanol. Besides the cluster $[(PPh_3)_2PtB_{10}H_{10}$-8,10-$(OEt)_2]\cdot CH_2Cl_2$ **(1)**,[10] we also obtained a previously unreported cluster: $[(PPh_3)_2PtB_{10}H_{11}$-11-OEt$]\cdot CH_2Cl_2$ **(2)**. When the reaction of *closo*-$B_{10}H_{10}^{2-}$ with $[PtCl_2(PPh_3)_2]$ in ethanol was carried out using solvothermal techniques, a novel $B_{10}H_{10}^{2-}$ deboronated *nido* 11-vertex diplatinaundecaborane $[(\mu$-$PPh_2)(PPh_3)_2Pt_2B_9H_6$-3,9,11-$(OEt)_3]\cdot CH_2Cl_2$ **(3)** was obtained. Clusters **1**–**3** were characterized by infrared spectroscopy, NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction.

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EXPERIMENTAL

Materials

The $(Et_3HN)_2B_{10}H_{10}$ was obtained from Professor Vladimir I. Bregadze (Institute of Organoelement Compounds, Russian Academy of Sciences) and $[PtCl_2(PPh_3)_2]$[13] was prepared by the reaction of an aqueous solution of K_2PtCl_4 with an ethanolic solution of PPh_3. Ethanol was distilled from CaH_2 prior to use. Petroleum ether refers to that fraction with a boiling point of 60–90 °C. *n*-Pentane and dichloromethane were purchased and used as received. Chromatography columns were packed with silica gel (60–200 mesh). All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen with the rigid exclusion of air and moisture. Some subsequent manipulations were performed in the air.

Measurements

Fourier transform infrared spectra were measured on a Nicolet-460 FTIR spectrophotometer in the range 4000–400 cm^{-1} as KBr pellets. Elemental analyses (C, H) were performed on a Perkin-Elmer 2400 II CHN elemental analyser. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard at 400.15 and 100.63 MHz, respectively. The spectra were acquired at room temperature (298 K) unless specified otherwise. 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.

Preparation of $[(PPh_3)_2PtB_{10}H_{10}$-8,10-$(OEt)_2]\cdot CH_2Cl_2$ (1) and $[(PPh_3)_2PtB_{10}H_{11}$-11-OEt]$\cdot CH_2Cl_2$ (2)

The reaction of $(Et_3HN)_2B_{10}H_{10}$ (0.28 g, 0.8 mmol) with $[PtCl_2(PPh_3)_2]$ (0.317 g, 0.4 mmol) in 50 ml of ethanol under reflux for 132 h under an atmosphere of dry nitrogen yields a deep-yellow solution. The solution was evaporated to dryness, redissolved in 5 ml of CH_2Cl_2 and chromatographed using dichloromethane–petroleum (4 : 1) as the eluting medium to give the two compounds **1** and **2**. Cluster **1**: $[(PPh_3)_2PtB_{10}H_{10}$-**8**,10-$(OEt)_2]\cdot CH_2Cl_2$ ($R_f = 0.39$, 233 mg, 39.03%), FTIR ν_{KBr}(cm^{-1}): 3055m, 2524s, 1636m, 1436s, 1202m, 1093s, 695s, 524s. ^1H NMR (400.15 MHz, $CDCl_3$): δ 0.986 ppm (6H), 4.181 ppm (4H); ^{13}C NMR (100.63 MHz, $CDCl_3$): δ 16.101 ppm, 16.947 ppm (2C), 77.000 ppm (2C). Anal. calc. for $C_{41}H_{52}B_{10}Cl_2O_2P_2Pt$: C, 48.62; H, 5.13; found: C, 48.47; H, 4.98%. Cluster **2**: $[(PPh_3)_2PtB_{10}H_{11}$-11-OEt]$\cdot CH_2Cl_2$ ($R_f = 0.76$, 21 mg, 3.52%), FTIR ν_{KBr}(cm^{-1}): 2921m, 2523s, 1635m, 1435s, 1215m, 1096s, 696s, 521s. ^1H NMR (400.15 MHz, $CDCl_3$):

Table 1. X-ray diffraction data for clusters **1–3**

Crystal data	**1**	**2**	**3**
Empirical formula	$C_{41}H_{52}B_{10}Cl_2O_2P_2Pt$	$C_{39}H_{48}B_{10}Cl_2OP_2Pt$	$C_{55}H_{63}B_9Cl_2O_3P_3Pt_2$
Formula weight	1012.86	968.80	1423.33
Crystal size (mm)	0.48 × 0.43 × 0.35	0.48 × 0.41 × 0.31	0.28 × 0.19 × 0.17
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/c	*P*2(1)/c	*P*2(1)/c
a (Å)	23.061(7)	10.226(4)	15.540(16)
b (Å)	11.481(4)	18.276(7)	15.260(16)
c (Å)	35.607(11)	23.519(9)	24.30(2)
α (°)	90	90	90
β (°)	106.902(4)	91.396(6)	95.27(3)
γ (°)	90	90	90
V(Å^3)	9020(5)	4394(3)	5738(10)
Z	8	4	4
D(Mg m^{-3})	1.489	1.461	1.648
F(000)	4032	1920	2788
Theta range (°)	1.89–25.03	1.73–25.03	1.87–25.05
Reflection collected	22 956	22 354	13 717
Independent reflection	7963	7736	9291
Goodness-of-fit on *F*	1.004	1.016	1.001
$R[I > 2\sigma(I)]$	$R_1 = 0.0508$	$R_1 = 0.0572$	$R_1 = 0.0468$
	$wR_2 = 0.1266$	$wR_2 = 0.1424$	$wR_2 = 0.0914$
R(all data)	$R_1 = 0.0654$	$R_1 = 0.0918$	$R_1 = 0.0866$
	$wR_2 = 0.1338$	$wR_2 = 0.1627$	$wR_2 = 0.1034$
Largest diff. peak and hole ($\times 10^2$ electrons Å^{-3})	1.641 and −1.316	2.967 and −2.137	2.232 and −2.177

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for cluster **1**

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Pt(7)	3483(1)	2998(1)	1175(1)	21(1)	C(13)	3328(3)	105(7)	846(2)	28(2)
B(1)	2293(4)	4929(9)	930(3)	38(2)	C(14)	2937(4)	610(8)	524(2)	39(2)
B(2)	2547(4)	3564(9)	833(3)	30(2)	C(15)	2711(5)	−17(9)	176(3)	56(3)
B(3)	3092(5)	4768(8)	998(3)	36(2)	C(16)	2875(5)	−1167(10)	153(3)	61(3)
B(4)	2829(4)	5607(9)	1332(3)	37(2)	C(17)	3262(5)	−1689(9)	482(3)	58(3)
B(5)	2180(4)	4853(9)	1395(3)	35(2)	C(18)	3502(4)	−1060(8)	827(3)	41(2)
B(6)	1975(4)	3662(9)	1064(3)	34(2)	C(19)	4516(4)	2662(6)	680(2)	26(2)
B(8)	3482(4)	4724(8)	1521(3)	27(2)	C(20)	3990(4)	2440(8)	378(2)	38(2)
B(9)	2875(5)	4708(9)	1766(3)	37(2)	C(21)	4019(5)	1794(10)	52(3)	60(3)
B(10)	2290(4)	3430(8)	1585(3)	29(2)	C(22)	4555(5)	1417(9)	22(3)	56(3)
B(11)	2521(4)	2547(8)	1213(2)	20(2)	C(23)	5078(5)	1657(9)	313(3)	53(3)
Cl(1)	3309(2)	6872(4)	9221(2)	127(2)	C(24)	5063(4)	2286(7)	642(3)	41(2)
Cl(2)	4032(2)	4783(4)	9415(1)	121(2)	C(25)	5107(3)	3338(7)	1507(2)	29(2)
O(1)	4055(3)	5046(6)	1694(2)	54(2)	C(26)	5060(4)	2969(8)	1865(2)	38(2)
O(2)	2008(3)	3027(5)	1851(2)	37(1)	C(27)	5562(5)	2906(10)	2187(3)	59(3)
P(1)	3665(1)	956(2)	1294(1)	24(1)	C(28)	6119(5)	3216(9)	2156(3)	59(3)
P(2)	4427(1)	3519(2)	1094(1)	23(1)	C(29)	6172(4)	3583(10)	1808(3)	60(3)
C(1)	3332(3)	388(7)	1667(2)	23(2)	C(30)	5671(4)	3655(8)	1483(3)	44(2)
C(2)	3400(4)	1014(8)	2008(2)	36(2)	C(31)	4538(3)	5002(7)	933(2)	33(2)
C(3)	3216(4)	571(9)	2314(3)	43(2)	C(32)	4807(4)	5859(8)	1210(3)	48(2)
C(4)	2946(4)	−518(9)	2280(3)	48(2)	C(33)	4899(5)	6933(9)	1087(4)	66(3)
C(5)	2873(4)	−1140(9)	1939(3)	47(2)	C(34)	4751(6)	7235(9)	698(4)	69(4)
C(6)	3065(4)	−711(7)	1632(2)	35(2)	C(35)	4500(6)	6389(9)	421(4)	68(3)
C(7)	4435(3)	376(6)	1459(2)	25(2)	C(36)	4400(5)	5299(9)	544(3)	51(3)
C(8)	4703(4)	136(8)	1856(3)	41(2)	C(37)	4243(6)	5619(13)	2070(4)	89(4)
C(9)	5312(4)	−232(10)	1980(3)	54(3)	C(38)	4316(11)	6845(13)	2058(6)	149(9)
C(10)	5636(4)	−306(8)	1713(3)	50(3)	C(39)	1687(5)	1928(9)	1778(3)	52(3)
C(11)	5372(4)	−47(8)	1327(3)	46(2)	C(40)	1407(7)	1716(10)	2101(4)	80(4)
C(12)	4772(3)	284(7)	1200(2)	30(2)	C(41)	3352(6)	5438(12)	9295(7)	181(11)

δ 0.864 ppm (3H), 1.564 ppm (2H): ^{13}C NMR (100.63 MHz, $CDCl_3$): 31.922 ppm (1C), 77.198 ppm (1C). Anal. calc. for $C_{39}H_{48}B_{10}Cl_2OP_2Pt$: C, 48.35; H,4.96; found: C, 48.09; H, 4.88%. Single crystals of clusters **1** and **2** suitable for X-ray diffraction were obtained from an *n*-pentane–dichloromethane solution.

Preparation of [(μ-PPh$_2$)(PPh$_3$)$_2$Pt$_2$B$_9$H$_6$-3,9,11-(OEt)$_3$]·CH$_2$Cl$_2$ (3)

$(Et_3HN)_2B_{10}H_{10}$ (0.28 g, 0.8 mmol), $[PtCl_2(PPh_3)_2]$ (0.317 g, 0.4 mmol) and 25 ml of distilled ethanol were mixed in a Teflon-lined autoclave in a dry nitrogen atmosphere and then maintained at 170 °C for 96 h, followed by slow cooling to room temperature. Thin-layer chromatographic separation (silica G; CH_2Cl_2-light petroleum, 4 : 1) gave cluster **3:** [(μ-PPh$_2$)(PPh$_3$)$_2$Pt$_2$B$_9$H$_6$-3,9,11-(OEt)$_3$]·CH$_2$Cl$_2$ (R_f = 0.38, 27 mg, 4.52%), FTIR ν_{KBr} (cm^{-1}): 2919s, 2505s, 1618w, 1434s, 1228m, 1095s, 686s, 519s. ^{1}H NMR (400.15 MHz, $CDCl_3$): δ 0.665 ppm (3H), 0.874 ppm (6H), 3.805 ppm (6H); ^{13}C NMR (100.63 MHz, $CDCl_3$): 29.689 ppm (3C), 77.000 ppm (3C). Anal. calc. for $C_{55}H_{63}B_9Cl_2O_3P_3Pt_2$: C, 46.41; H, 4.43; found: C, 46.82; H, 4.42%. Single crystal of cluster **3** suitable for X-ray diffraction were obtained from an *n*-pentane–dichloromethane solution.

X-ray structure determination

The collection of crystallographic data for complexes **1–3** was carried out on a Bruker Smart-1000 CCD diffractometer using graphite-monochromatized Mo Kα (λ = 0.71073 Å) at 298(2) K. The structures were solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package.[14] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. Details of the crystal parameters, data collection and refinement are summarized in Table 1. Atomic coordinates and equivalent isotropic displacement parameters of clusters **1–3** are shown in Tables 2–4.

RESULTS AND DISCUSSION

Synthesis and characterization

During refluxing, as described by Hawthorne[11] in the reaction of *closo*-$B_{10}H_{10}^{2-}$ with $[PtCl_2(PPh_3)_2]$ in ethanol, the $B_{10}H_{10}^{2-}$

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for cluster **2**

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Pt(7)	2372(1)	3026(1)	1982(1)	20(1)	C(13)	3750(10)	3987(5)	732(4)	28(2)
B(1)	1388(13)	2644(7)	3333(5)	33(3)	C(14)	2772(12)	4190(6)	356(4)	42(3)
B(2)	1373(11)	2332(6)	2617(5)	27(3)	C(15)	2959(13)	4171(7)	−233(4)	53(4)
B(3)	1411(11)	3305(6)	2790(5)	25(2)	C(16)	4096(17)	3949(8)	−424(5)	64(4)
B(4)	2339(12)	3445(7)	3419(5)	29(3)	C(17)	5122(15)	3763(8)	−67(5)	63(4)
B(5)	2960(15)	2584(7)	3610(5)	43(4)	C(18)	4950(12)	3773(6)	507(5)	47(3)
B(6)	2333(14)	1892(7)	3163(5)	35(3)	C(19)	637(10)	2956(5)	741(4)	32(2)
B(8)	2988(12)	3720(7)	2763(4)	29(3)	C(20)	−92(11)	3494(6)	1005(5)	41(3)
B(9)	3984(14)	3211(7)	3290(5)	39(3)	C(21)	−883(13)	3966(7)	690(6)	60(4)
B(10)	4008(14)	2181(7)	3127(6)	43(3)	C(22)	−949(14)	3916(8)	107(6)	67(4)
B(11)	3002(12)	1953(6)	2472(5)	31(3)	C(23)	−175(16)	3403(9)	−165(6)	70(4)
O(1)	3270(7)	1417(4)	2095(3)	39(2)	C(24)	575(12)	2900(6)	159(5)	44(3)
Cl(1)	8643(10)	4137(7)	4892(5)	138(5)	C(25)	2721(11)	1866(6)	734(4)	33(3)
Cl(2)	7692(10)	3501(9)	3885(5)	173(7)	C(26)	4030(11)	2074(6)	755(5)	41(3)
P(1)	3450(2)	3983(1)	1499(1)	23(1)	C(27)	4894(15)	1752(8)	388(7)	70(4)
P(2)	1584(3)	2331(1)	1197(1)	25(1)	C(28)	4478(17)	1224(9)	19(6)	72(5)
C(1)	5127(9)	4035(6)	1801(4)	26(2)	C(29)	3211(17)	1025(8)	−1(5)	64(4)
C(2)	5818(11)	4682(6)	1875(5)	41(3)	C(30)	2298(13)	1336(7)	353(5)	51(3)
C(3)	5762(11)	3379(6)	1929(5)	40(3)	C(31)	361(11)	1628(6)	1338(4)	33(3)
C(4)	7027(12)	3383(8)	2136(5)	52(3)	C(32)	−978(13)	1803(7)	1322(6)	54(3)
C(5)	7670(11)	4054(9)	2211(6)	62(4)	C(33)	−1871(13)	1265(8)	1428(6)	70(4)
C(6)	7096(13)	4698(8)	2079(6)	62(4)	C(34)	−1517(15)	561(8)	1567(6)	69(4)
C(7)	2675(9)	4876(5)	1574(4)	23(2)	C(35)	−219(16)	406(7)	1590(5)	63(4)
C(8)	1543(11)	4965(6)	1888(4)	37(3)	C(36)	746(12)	921(6)	1482(5)	44(3)
C(9)	940(12)	5635(6)	1928(5)	48(3)	C(37)	4541(12)	1120(6)	2060(5)	52(3)
C(10)	1489(12)	6243(6)	1677(5)	45(3)	C(38)	4505(14)	466(7)	1664(5)	61(4)
C(11)	2594(12)	6168(6)	1365(5)	41(3)	C(39)	8980(20)	3759(19)	4284(9)	124(18)
C(12)	3185(10)	5476(6)	1296(4)	36(3)					

ion is attacked by a formal $\{(PPh_3)_2Pt^{2+}\}$ moiety along an apical–equatorial edge. Bond rupture of boron atom sets 1, 2; 2, 5; 5, 9; 8, 9 then occurs, with the subsequent attack of ethanol. The reverse attack sequence, i.e. initial attack by ethanol and then cage opening, could also have occurred or, in the limiting case, these processes could have been concurrent. In any case, attack of ethanol would probably be at one of the boron atoms 1, 2, 5, 8, 9 or 10 of the open face. Thus, ethoxy substitution would have occurred at boron 2, 3, 8, 9, 10 or 11, resulting in the formation of three sets of positional isomers with each set containing a *d,l*-enantiomeric pair. The double ethoxy substitution for $[(PPh_3)_2PtB_{10}H_{10}$-8,10-$(OEt)_2]\cdot CH_2Cl_2$ (**1**)[10] occurred at the boron 8 and 10 positions and the single ethoxy substitution for $[(PPh_3)_2PtB_{10}H_{11}$-11-OEt$]\cdot CH_2Cl_2$ (**2**) occurred at the boron 11 position.

To our knowledge there are no reports on the preparation of metallaborane using hydro(solvo)thermal techniques during which the reaction temperature, which is greater than the boiling point of the solvents, can be reached typically under autogenous pressure.[15,16] We have explored hydro(solvo)thermal techniques by introducing the strategy to the synthesis of metallaborane to obtain two

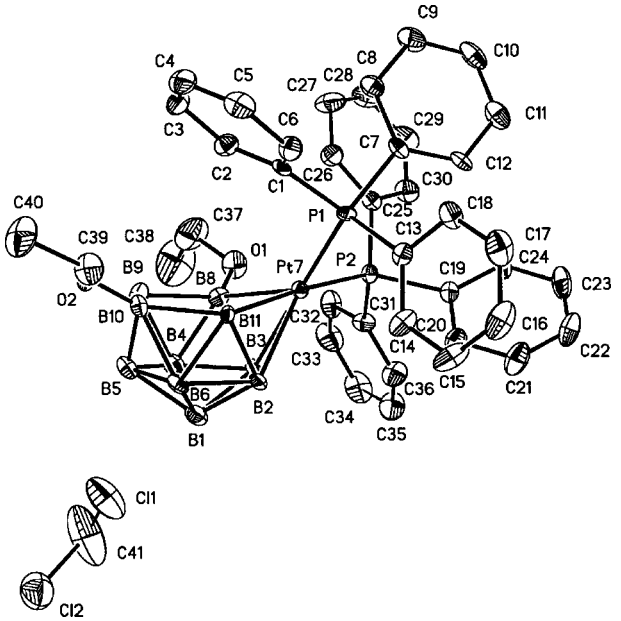

Figure 1. Crystal structure of cluster **1**.

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for cluster **3**

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Pt(7)	2116(1)	8355(1)	1684(1)	22(1)	C(19)	1435(7)	10 338(6)	1204(4)	31(3)
Pt(8)	3053(1)	7047(1)	1349(1)	22(1)	C(20)	1940(7)	11 067(7)	1322(5)	47(3)
B(1)	3425(7)	7375(7)	2727(4)	28(3)	C(21)	2177(8)	11 609(8)	895(7)	72(4)
B(2)	2638(7)	8218(7)	2570(4)	26(3)	C(22)	1902(10)	11 438(10)	371(6)	71(4)
B(3)	3455(8)	7886(8)	2096(4)	33(3)	C(23)	1397(9)	10 730(9)	240(5)	61(4)
B(4)	3649(7)	6686(7)	2189(4)	25(3)	C(24)	1172(7)	10 195(7)	642(5)	46(3)
B(5)	2920(8)	6329(8)	2662(5)	30(3)	C(25)	35(6)	9350(7)	1483(4)	30(3)
B(6)	2350(8)	7248(7)	2907(5)	34(3)	C(26)	−516(7)	10 064(7)	1421(4)	38(3)
B(9)	2696(8)	6093(7)	1968(5)	33(3)	C(27)	−1373(7)	9961(8)	1292(4)	46(3)
B(10)	1800(7)	6508(7)	2456(4)	27(3)	C(28)	−1711(7)	9147(9)	1217(5)	54(4)
B(11)	1617(8)	7733(8)	2432(4)	29(3)	C(29)	−1184(8)	8424(8)	1257(5)	55(4)
Cl(1)	3848(3)	1656(3)	2310(2)	103(2)	C(30)	−308(7)	8510(7)	1405(4)	40(3)
Cl(2)	3154(3)	3064(3)	2909(2)	106(2)	C(31)	3267(7)	6013(6)	106(4)	29(3)
O(1)	4146(4)	8390(4)	1964(3)	32(2)	C(32)	2408(7)	5766(7)	28(4)	37(3)
O(2)	2489(4)	5344(4)	1697(3)	38(2)	C(33)	1979(7)	5718(7)	−491(5)	48(3)
O(3)	815(5)	8064(5)	2499(3)	43(2)	C(34)	2411(8)	5936(7)	−947(4)	48(3)
P(1)	2209(2)	7963(2)	786(1)	26(1)	C(35)	3261(8)	6175(7)	−869(4)	44(3)
P(2)	1182(2)	9510(2)	1695(1)	25(1)	C(36)	3697(7)	6226(6)	−354(4)	34(3)
P(3)	3758(2)	6108(2)	804(1)	26(1)	C(37)	3992(7)	4964(6)	993(4)	30(3)
C(1)	2726(6)	8610(6)	289(4)	24(2)	C(38)	4397(7)	4768(7)	1507(4)	44(3)
C(2)	3163(7)	9343(7)	436(4)	41(3)	C(39)	4633(8)	3918(8)	1639(5)	49(3)
C(3)	3642(8)	9792(8)	79(6)	59(4)	C(40)	4459(7)	3259(7)	1265(5)	48(3)
C(4)	3727(8)	9452(9)	−431(5)	61(4)	C(41)	4057(7)	3440(7)	764(4)	43(3)
C(5)	3298(8)	8709(8)	−595(5)	54(3)	C(42)	3818(7)	4293(7)	628(4)	40(3)
C(6)	2795(7)	8275(7)	−248(4)	39(3)	C(43)	4821(6)	6576(6)	750(3)	26(2)
C(7)	1241(6)	7495(8)	437(4)	35(3)	C(44)	4888(8)	7471(7)	689(4)	42(3)
C(8)	881(7)	6746(8)	663(5)	50(3)	C(45)	5687(9)	7855(8)	638(5)	60(4)
C(9)	139(9)	6372(9)	427(5)	67(4)	C(46)	6420(8)	7355(10)	667(5)	56(4)
C(10)	−282(9)	6723(12)	−34(7)	87(5)	C(47)	6364(7)	6467(9)	726(4)	51(3)
C(11)	59(9)	7462(12)	−260(6)	78(5)	C(48)	5570(7)	6079(7)	761(4)	33(3)
C(12)	793(7)	7840(8)	−20(4)	47(3)	C(49)	4105(7)	9320(6)	1972(5)	42(3)
C(13)	1187(6)	10 080(6)	2357(4)	23(2)	C(50)	4874(8)	9690(7)	1730(5)	65(4)
C(14)	1955(7)	10 396(7)	2589(4)	41(3)	C(51)	2020(9)	4650(8)	1889(6)	75(5)
C(15)	2019(8)	10 814(7)	3093(5)	48(3)	C(52)	1916(12)	3959(12)	1502(7)	137(7)
C(16)	1296(9)	10 903(7)	3362(5)	51(3)	C(53)	100(10)	7632(10)	2726(6)	100(6)
C(17)	509(8)	10 561(7)	3157(4)	50(3)	C(54)	163(15)	7707(15)	3301(8)	224(13)
C(18)	467(7)	10 159(7)	2638(4)	38(3)	C(55)	4028(7)	2381(8)	2846(5)	64(4)

novel clusters: $[(PPh_3)_2(\mu\text{-}PPh_2)Pt_2B_9H_6\text{-}3,10,11\text{-}(O\mathit{i}Pr)_3]$ and $[(PPh_3)_2(\mu\text{-}PPh_2)Pt_2B_9H_6\text{-}3,10\text{-}(O\mathit{i}Pr)_2\text{-}11\text{-}Cl]$.[17]

Clusters **1–3** were characterized by spectroscopic data and elemental analyses. The IR spectra of the three clusters exhibited absorptions characteristic of terminal B–H vibrations at 2524, 2523 and 2505 cm^{-1}, respectively. Absorptions characteristic of the phenyl moiety were observed, and strong and broad absorptions at ca. 1215 cm^{-1} were assigned to B–O stretching modes. There are three or four peaks from 1630 to 1430 cm^{-1} that can be assigned to $\nu_{C=C}$ stretching vibrations. The peak at 1100 cm^{-1} is $\nu_{P\text{-}C}$ and that at 545–490 cm^{-1} is $\delta_{P\text{-}C}$. These peaks indicate that PPh_3 ligands are retained in clusters.[18]

The ^1H NMR spectra (400.15 MHz) of clusters **1–3** display complex patterns at about $\delta = 7.0$ that can be attributed to the phosphine ligands. The resonance at around $\delta = 0.8$ can be assigned to the ethoxy methyl protons. In the ^{13}C NMR spectra (100.63 MHz) the resonance at about $\delta = 30.0$ can be assigned to the ethoxy methyl C atoms and that at $\delta = 70.0$ can be assigned to the ethoxy methylene C atoms.

Crystal structure

Crystal structures of clusters **1** and **2** are shown in Figs 1 and 2. Selected bond lengths and angles are given in Table 5. Each of clusters **1** and **2** co-crystallizes with one molecule of CH_2Cl_2 per formula unit. They all have

a *nido* 11-vertex {PtB_{10}} polyhedral skeleton in which the Pt atom lies in the open PtB_4 face. Each Pt atom connects with four B atoms, and Pt–B distances vary in the range 2.237(9)–2.333(9) Å and 2.219(11)–2.356(10) Å, respectively, which are similar to those in clusters [7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{12}$][18] and [8-Cl-7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{11}$][19] [2.214(5)–2.301(6) Å and 2.206(12)-2.342(13) Å]. Each Pt atom is connected with two P atoms of PPh_3 and the average Pt–P bond lengths are 2.377(2) Å and 2.370(3) Å, respectively, which are analogous to the corresponding bond lengths in $Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2$ [2.252(4) Å].[20] The range of bond lengths of B(8)–B(9) [1.838(16)–1.854(14) Å], B(9)–B(10) [1.921(18)–1.970(14) Å] and B(10)–B(11) [1.865(12)–1.879(18) Å] are analogous to the corresponding bond lengths in unsubstituted cluster *nido*-[7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{12}$] [1.809(9), 1.976(9) and 1.841(8) Å].[18] The H atoms at positions B(8) and B(10) were substituted by two ethoxyl groups in cluster **1**. Cluster **2** exhibited similar behaviour at position B(11). The average B–O bond lengths are 1.355 Å, similar to those in $(PPh_3)_2Pt[SB_8H_9(OEt)]$ [1.476(24) Å][21] and $[Pt(SePh)(PEt_3)\{\eta^5\text{-}8\text{-}O(CH_2)_4Cl\text{-}7\text{-}CB_{10}H_{10}\}]$ [1.369(7) Å].[22]

The crystal structure of cluster **3** is shown in Fig. 3 and selected bond lengths and angles are given in Table 5. Cluster **3** also co-crystallizes with one molecule of CH_2Cl_2 per formula unit. It has a *nido* 11-vertex {Pt_2B_9} polyhedral skeleton, with two Pt atoms in neighbouring positions of the open Pt_2B_3 face. There is a PPh_2 group bridging two Pt atoms, which are seldom reported in metallaborane chemistry. The Pt–Pt distances [2.643(2) Å] are considerably shorter than the Pt–Pt distances in $Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2$ [3.0744 Å][20] and shorter than the Pt–Pt distances in diplatinaborane $[(PMe_2Ph)_3ClPt_2B_{10}H_9(PMe_2Ph)]$ [2.863 Å][23] but analogous to those in $[Pt_2(\mu\text{-}\eta^3 - nido\text{-}B_6H_9)_2(PMe_2Ph)_2]$ [2.644(1) Å][24] and $[(PMe_2Ph)_2(Pt_2B_8H_{14})]$ [2.621(1) Å].[25] The Pt(7)–P(1) and Pt(8)–P(1) bond lengths are 2.279(3) Å and 2.284(3) Å, which are similar to those in clusters **1** and **2**. The Pt(7)–P(1)–Pt(8)

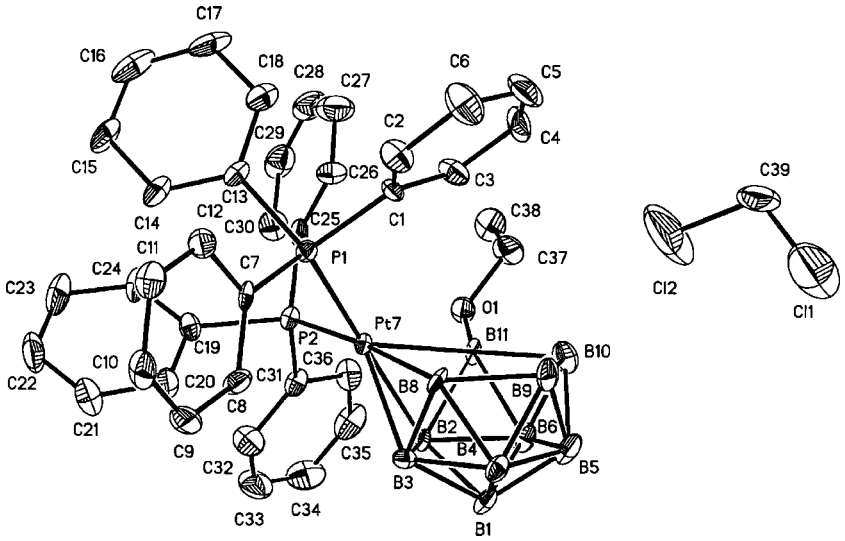

Figure 2. Crystal structure of cluster **2**.

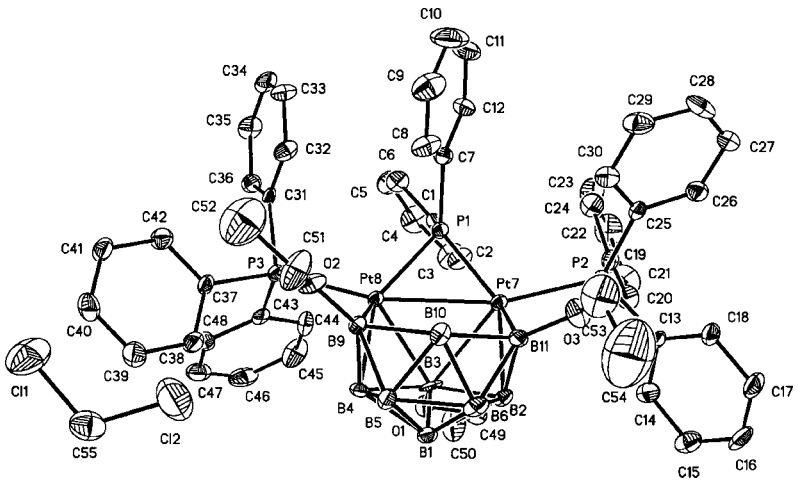

Figure 3. Crystal structure of cluster **3**.

Table 5. Selected bond lengths (Å) and angles (°) of clusters **1**, **2** and **3**

	1		2		3
Pt(7)–B(3)	2.237(9)	Pt(7)–B(3)	2.219(11)	Pt(7)–B(2)	2.241(11)
Pt(7)–B(2)	2.243(8)	Pt(7)–B(2)	2.225(10)	Pt(7)–B(11)	2.252(12)
Pt(7)–B(11)	2.320(8)	Pt(7)–B(11)	2.356(10)	Pt(7)–B(3)	2.337(12)
Pt(7)–B(8)	2.333(9)	Pt(7)–B(8)	2.307(11)	Pt(7)–P(1)	2.279(3)
Pt(7)–P(2)	2.355(2)	Pt(7)–P(2)	2.366(3)	Pt(7)–P(2)	2.285(3)
Pt(7)–P(1)	2.398(2)	Pt(7)–P(1)	2.373(3)	Pt(7)–Pt(8)	2.643(2)
O(1)–B(8)	1.337(10)	O(1)–B(11)	1.353(14)	Pt(8)–B(9)	2.201(13)
O(1)–B(10)	1.375(11)	O(2)–C(37)	1.413(13)	Pt(8)–B(3)	2.262(11)
B(8)–B(9)	1.854(14)	B(8)–B(9)	1.838(16)	Pt(8)–B(4)	2.230(10)
B(9)–B(10)	1.970(14)	B(9)–B(10)	1.921(18)	Pt(8)–P(1)	2.284(3)
B(10)–B(11)	1.865(12)	B(10)–B(11)	1.879(18)	Pt(8)–P(3)	2.296(3)
B(4)–B(8)	1.779(13)	B(2)–B(11)	1.845(16)	O(1)–B(3)	1.381(13)
B(5)–B(10)	1.759(14)	B(6)–B(11)	1.783(17)	O(2)–B(9)	1.344(12)
B(1)–B(3)	1.796(13)	B(1)–B(3)	1.759(16)	O(3)–B(11)	1.368(13)
B(3)–Pt(7)–B(2)	48.6(4)	B(3)–Pt(7)–B(2)	48.6(4)	B(2)–Pt(7)–B(11)	46.0(4)
B(3)–Pt(7)–B(11)	84.6(3)	B(3)–Pt(7)–B(11)	84.6(3)	B(2)–Pt(7)–B(3)	47.9(4)
B(2)–Pt(7)–B(11)	46.5(3)	B(2)–Pt(7)–B(11)	46.5(3)	B(3)–Pt(7)–B(11)	83.3(4)
B(3)–Pt(7)–B(8)	46.8(3)	B(3)–Pt(7)–B(8)	46.8(3)	B(2)–Pt(7)–Pt(8)	93.6(3)
B(2)–Pt(7)–B(8)	83.9(3)	B(2)–Pt(7)–B(8)	83.9(3)	B(11)–Pt(7)–Pt(8)	99.8(3)
B(11)–Pt(7)–B(8)	90.7(3)	B(11)–Pt(7)–B(8)	90.7(3)	B(3)–Pt(7)–Pt(8)	53.6(3)
B(1)–B(2)–Pt(7)	118.6(6)	B(1)–B(2)–Pt(7)	118.6(6)	B(9)–Pt(8)–B(4)	47.2(4)
B(6)–B(2)–Pt(7)	120.0(5)	B(6)–B(2)–Pt(7)	120.0(5)	B(9)–Pt(8)–B(3)	84.0(4)
B(11)–B(2)–Pt(7)	69.0(4)	B(11)–B(2)–Pt(7)	69.0(4)	B(4)–Pt(8)–B(3)	49.1(4)
B(3)–B(2)–Pt(7)	65.5(4)	B(3)–B(2)–Pt(7)	65.5(4)	B(9)–Pt(8)–Pt(7)	96.2(3)
B(1)–B(3)–Pt(7)	116.4(6)	B(1)–B(3)–Pt(7)	116.4(6)	B(4)–Pt(8)–Pt(7)	95.7(3)
B(4)–B(3)–Pt(7)	119.6(6)	B(4)–B(3)–Pt(7)	119.6(6)	B(3)–Pt(8)–Pt(7)	56.3(3)
B(8)–B(3)–Pt(7)	69.4(4)	B(8)–B(3)–Pt(7)	69.4(4)	B(11)–B(2)–Pt(7)	67.3(5)
B(2)–B(3)–Pt(7)	65.9(4)	B(2)–B(3)–Pt(7)	65.9(4)	B(6)–B(2)–Pt(7)	116.0(6)
B(4)–B(8)–Pt(7)	114.5(5)	B(4)–B(8)–Pt(7)	114.5(5)	B(1)–B(2)–Pt(7)	116.8(7)
B(3)–B(8)–Pt(7)	63.8(4)	B(3)–B(8)–Pt(7)	63.8(4)	B(3)–B(2)–Pt(7)	68.8(5)
B(9)–B(8)–Pt(7)	110.9(5)	B(9)–B(8)–Pt(7)	110.9(5)	B(1)–B(3)–Pt(8)	115.4(7)
B(6)–B(11)–Pt(7)	115.5(5)	B(6)–B(11)–Pt(7)	115.5(5)	B(2)–B(3)–Pt(8)	119.8(6)
B(2)–B(11)–Pt(7)	64.5(4)	B(2)–B(11)–Pt(7)	64.5(4)	B(4)–B(3)–Pt(8)	64.6(5)
B(10)–B(11)–Pt(7)	113.3(5)	B(10)–B(11)–Pt(7)	113.3(5)	B(1)–B(3)–Pt(7)	115.1(7)

angle [70.79(9)°] was smaller than the corresponding Pt–P–Pt angle in $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ [average 86.1(1)°].[20] Each Pt atom also connects with one PPh_3 and three B atoms. The bond lengths of Pt(7)–P(2) and Pt(8)–P(3) are 2.285(3) Å and 2.296(3) Å, which are slightly longer than the Pt(7)–P(1) and Pt(8)–P(1) bond lengths. The H atoms at positions B(3), B(9) and B(11) are substituted by three ethoxyl groups and the B–O distances are 1.381(13), 1.344(12) and 1.368(13) Å, respectively, similar to those in clusters **1** and **2**.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 233 525, 233 524 and 233 526 for clusters **1–3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223 336 033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk].

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