A New Strategy for the Preparation of Metallaboranes − Solvothermal Synthesis and Structural Characterisation of Two Nido 11-vertex Diplatinaundecaborane Clusters

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Two novel nido 11-vertex diplatinaundecaborane clusters $[(\mu\text{-}PPh_2)(PPh_3)_2Pt_2B_9H_6Cl(O\textit{i}Pr)_2]$ (**1**) and $[(\mu\text{-}PPh_2)(PPh_3)_2Pt_2B_9H_6(O\textit{i}Pr)_3]$ (**2**) have been solvothermally synthesised and characterised by elemental analysis, IR, Raman, ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction. The latter analysis revealed that two Pt atoms remain in neighbouring positions of the open Pt_2B_3 face in both clusters which were markedly different from the products obtained from the identical starting mixture under refluxing conditions.

Introduction

Hydro(solvo)thermal techniques were originally developed by geochemists to mimic the conditions of mineral growth. They involve heating reaction mixtures in a sealed vessel such that reaction temperatures greater than the boiling point of the solvent can be reached, typically under autogenous pressure. The temperature regime available in hydro(solvo)thermal techniques, intermediate between low-temperature solution chemistry and high-temperature solid-state chemistry, can favour the formation of metastable kinetic rather than thermodynamic products. Recently, hydro(solvo)thermal techniques have attracted much attention in preparative chemistry[1] and have been employed extensively in the preparation of zeolites,[2] oxide and chalcogenide nanoparticles[3] as well as in the synthesis of molecular magnets[4] and coordination polymers.[5]

On the other hand, boron cluster chemistry has progressed considerably and developed into a fruitful area that includes boranes, carboranes, main group heteroboranes, metallaboranes, metallacarboranes and metallaheteroboranes. It has provided a lot of potentially useful applications, including boron neutron capture treatment (BNCT) of tumours, in solvent extractions, material science as well as in catalytic and host-guest chemistry.[6−8] The synthetic methods used to prepare metal-boron clusters are mostly conventional reactions at reflux temperature or cluster fusion processes.[9] To the best of our knowledge, there are no reports on the preparation of metallaboranes using hydro(solvo)thermal techniques in boron cluster chemistry. We have been exploring hydro(solvo)thermal techniques and introducing the strategy into the synthesis of metallaboranes. We now report two nido 11-vertex diplatinaundecaborane clusters $[(\mu\text{-}PPh_2)(PPh_3)_2Pt_2B_9H_6Cl(O\textit{i}Pr)_2]$ (**1**) and $[(\mu\text{-}PPh_2)(PPh_3)_2Pt_2B_9H_6(O\textit{i}Pr)_3]$ (**2**) prepared from the reaction of $[PtCl_2(PPh_3)_2]$ with $[B_{10}H_{10}]^{2-}$ in *i*PrOH under solvothermal conditions.

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Results and Discussion

X-ray structural analyses revealed that the structures of these two clusters are very similar except for the substituent groups at position 11 in each case. They both have a *nido*-eleven-vertex $\{Pt_2B_9\}$ polyhedral skeleton with two Pt atoms in neighbouring positions of the open Pt_2B_3 face. These are the first examples of nido 11-vertex diplatinaundecaborane clusters in metallaborane chemistry characterised by X-ray diffraction. There is a PPh_2 group bridging two Pt atoms and the Pt−Pt distances [2.6672(11) Å for **1**, 2.6357(8)Å for **2**] are shorter than the Pt−Pt distances in the diplatinaborane $[(PMe_2Ph)_3ClPt_2B_{10}H_9(PMe_2Ph)]$ (2.863Å)[10] and considerably shorter than the Pt−Pt distances in $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$[11] (average 3.0744Å) which also has a PPh_2 group as a bridging ligand. The Pt(7)−P(1) and Pt(8)−P(1) bond lengths are 2.314(4) Å in **1** and 2.2992(10) Å in **2**, and 2.299(4) Å in **1** and 2.3013(13) Å in **2**, respectively. The Pt(7)−P(1)−Pt(8) angle is 70.65(10)° in **1** and 69.91(3)° in **2**, values which are smaller than that in $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$[11] [average 86.1(1)°]. Each Pt atom is also connected to one PPh_3 group and three B atoms. The Pt−P bond lengths [2.298(4)−2.3208(10) Å] are similar to the reported Pt−P bond distances in $[(PMe_2Ph)_2PtB_{10}H_{12}]$[12] and $[(PMe_2Ph)_2PtB_{10}H_{11}Cl]$[13] [2.309(1)−2.354(3)Å]. The Pt−B bond lengths are consistent with the corresponding distances found in the related compound $[(PPh_3)(PhCOS)PtB_{10}H_{11}]$

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[2.263(19) Å].[14] A Cl atom remains at vertex 11 in cluster **1**, whereas a O*i*Pr group occupies the same position in cluster **2**. Both have two O*i*Pr group at positions 3 and 9. The bond lengths B−Cl [1.80(2) Å] and B−O [1.359(4)−1.393(4)Å] are in the ranges of the corresponding values in metallaborane clusters.[15]

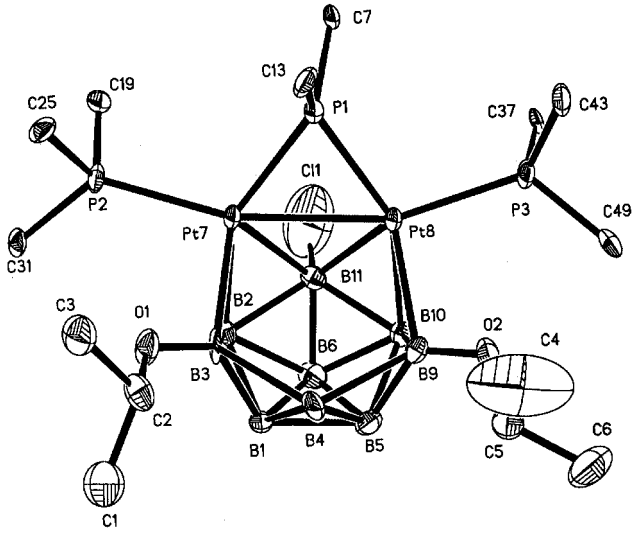

Figure 1. Molecular structure of **1** (H atoms omitted for clarity); selected bond lengths (Å) and angles (°): Pt(7)−Pt(8) 2.6672(11), Pt(7)−P(1) 2.314(4), Pt(8)−P(1) 2.298(4), Pt(7)−P(2) 2.319(4), Pt(8)−P(3) 2.299(4), Pt(7)−B(2) 2.242(16), Pt(7)−B(3) 2.258(19), Pt(7)−B(11) 2.244(16), Pt(8)−B(9) 2.248(18), Pt(8)−B(10) 2.260(15), Pt(8)−B(11) 2.252(16), B(3)−O(1) 1.355(18), B(9)−O(2) 1.38(2), B(11)−Cl(1) 1.80(2); Pt(8)−P(1)−Pt(7) 70.67(10), B(2)−Pt(7)−B(11) 48.4(6), B(2)−Pt(7)−B(3) 47.5(6), B(3)−Pt(7)−B(11) 81.7(6), B(9)−Pt(8)−B(10) 45.7(6), B(9)−Pt(8)−B(11) 82.0(7), B(11)−Pt(8)−B(10) 48.1(6).

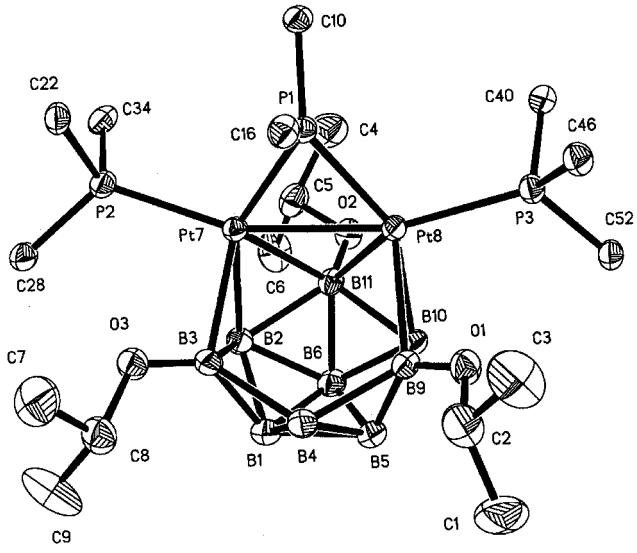

Figure 2. Molecular structure of **2** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Pt(7)−Pt(8) 2.6357(8), Pt(7)−P(1) 2.2992(10), Pt(8)−P(1) 2.3013(13), Pt(7)−P(2) 2.3208(10), Pt(8)−P(3) 2.3081(12), Pt(7)−B(2) 2.260(4), Pt(7)−B(3) 2.261(4), Pt(7)−B(11) 2.301(4), Pt(8)−B(9) 2.293(4), Pt(8)−B(10) 2.242(4), Pt(8)−B(11) 2.277(4), B(3)−O(3) 1.359(4), B(9)−O(1) 1.371(4), B(11)−O(2) 1.393(4); Pt(8)−P(1)−Pt(7) 69.91(3), B(2)−Pt(7)−B(11) 48.31(13), B(2)−Pt(7)−B(3) 46.44(14), B(3)−Pt(7)−B(11) 83.29(14), B(9)−Pt(8)−B(10) 46.37(15), B(9)−Pt(8)−B(11) 83.25(14), B(11)−Pt(8)−B(10) 49.03(13).

When the reaction of $[PtCl_2(PPh_3)_2]$ with $[B_{10}H_{10}]^{2-}$ in *i*PrOH takes place under conventional reflux conditions under a dry N_2 atmosphere, three nido 11-vertex platinaundecaborane clusters $[(PPh_3)_2PtB_{10}H_{10}$-8-O*i*Pr], $[(PPh_3)_2PtB_{10}H_{10}$-9-O*i*Pr] and $\{(PPh_3)_2PtB_{10}H_{10}$–8, 10-$(OiPr)_2\}$ are obtained.[16] These species are markedly different from the products obtained under solvothermal conditions. The reason for this may be attributed to the high temperature of the solvothermal reaction. Another example is that the reaction of $[RuCl_2(PPh_3)_3]$ with $[B_{10}H_{10}]^{2-}$ in glycol also yield two deboronated clusters $[(PPh_3)ClHRuB_9H_6(PPh_3)_2(OCH_2CH_2OH)]$ and $[(PPh_3)$-$ClHRuB_9H_5(OCH_2CH_2OH)_2(PPh_3)_2]$.[17] This illustrates that deboronation can be occur easily at high temperature. Another case of deboronation of $[B_{10}H_{10}]^{2-}$ can be included: trans-$[Ir(CO)Cl(PPh_3)_2]$ reacts with $[B_{10}H_{10}]^{2-}$ in methanol at reflux to yield $[\{IrC(OH)B_8H_6(OMe)\}$-$(C_6H_4PPh_2)(PPh_3)]$, $[(MeCOO)(PPh_3)\{HIrCB_8H_7(PPh_3)\}]$ and $[1,1,2$-$(CO)_3$-1-(PPh_3)-2,2-$(Ph_2P$-*ortho*-$C_6H_4)_2$-*closo*-$(1,2$-$Ir_2B_4H_2)]$.[18]

Conclusion

We have introduced solvothermal techniques into the preparation of metallaborane clusters for the first time and obtained two novel nido 11-vertex diplatinaundecaborane clusters, in which one boron atom was deboronated and two Pt atoms remain in neighbouring positions of the open Pt_2B_3 face in both clusters. The isolation of these two clusters suggests that temperature can control the result of the reaction.

Experimental Section

Materials and General Methods: All chemicals were commercially purchased and used without further purification except *i*PrOH which was dried with CaH_2. Elemental analyses (C, H and N) were performed with a Perkin−Elmer 2400 II Elemental Analyser. IR spectra were recorded in the range 400−4000cm^{-1} with an Nicolet-460 FT-IR spectrophotometer using KBr pellets. Raman spectra were acquired on a Renshaw RM2000 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian Mercury 400 (400 MHz) nuclear magnetic resonance instrument.

Synthesis of $[(\mu$-$PPh_2)(PPh_3)_2Pt_2B_9H_6Cl(OiPr)_2]$ (1) and $[(\mu$-$PPh_2)(PPh_3)_2Pt_2B_9H_6(OiPr)_3]$ (2): $(NEt_4)_2[B_{10}H_{10}]$ (303 mg, 8 mmol), $[PtCl_2(PPh_3)_2]$ (317 mg, 4 mmol) and distilled *i*PrOH (25 mL) were mixed in a Telfon lined autoclave under a dry N_2 atmosphere. The mixture was maintained at 170 °C for 96 h then slowly cooled to room temperature. TLC separation (silica G, CH_2Cl_2/light petroleum, 4:1) gave clusters **1** (R_f = 0.54, 18 mg, 2.9%) and **2** (R_f = 0.24, 77 mg, 12.4%). The single-crystals were obtained from an *n*-pentane/dichloromethane solution.

Cluster 1: $C_{54}H_{60}B_9ClO_2P_3Pt_2$ (M = 1356.85): calcd. C 47.80, H 4.42, found C 47.68, H 4.33. FT-IR (KBr): 3054 (m), 2970 (m), 2507 (vs), 1633 (s), 1434 (vs), 1234 (s), 1109 (s), 1095 (vs), 691 (s), 528 cm^{-1} (s).

Cluster 2: $C_{57}H_{67}B_9O_3P_3Pt_2$ (M = 1380.49): calcd. C 49.55, H 4.85, found C 49.13, H 4.56. FT-IR (KBr): 3050 (m), 2963 (m), 2509 (vs), 1634 (m), 1433 (s), 1382 (m), 1108 (vs), 691 cm^{-1} (vs); Raman: 3052.5 (m), 2513.8 (vs), 1583 (m), 1097 (m), 1000 (vs), 215 cm^{-1} (w). ^1H NMR (400.15 MHz, $CDCl_3$): δ = 0.659 (d, J = 6.0 Hz, 6 H, CH_3), 0.822 (d, J = 6.0 Hz, 6 H, CH_3), 1.101 (d, J = 6.4 Hz, 6 H, CH_3), 4.181 (7, J = 6.4 Hz, 1 H, CH), 4.462 ppm (7, J = 6.0 Hz, 2 H, CH). ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 23.452, 23.766, 25.475, (6 C, CH_3), 73.781 ppm (3 C, CH).

X-ray Crystallography: Data were collected on a Bruker SMART 1000 CCD diffractometer using Mo-K_α radiation. Both structures were solved by direct methods and subsequent Fourier difference techniques and then refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package. CCDC-245790 and -245791 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data for 1: $C_{54}H_{60}B_9ClO_2P_3Pt_2$, M = 1356.85, triclinic, space group $P\bar{1}$, a = 12.611(5), b = 13.469(5), c = 17.930(7) Å, α = 83.357(6), β = 75.989(6), γ = 67.832(5)°, V = 2735.40(18) Å^3, T = 293(2) K, Z = 2, $D_{calcd.}$ = 1.647 g/cm^3, crystal dimensions 0.38 × 0.27 × 0.17 mm, Mo-K_α radiation, λ = 0.71073 Å, R_1 = 0.0675, wR_2 = 0.1471 for 5531 reflections with $I > 2\sigma(I)$, and R_1 = 0.1197, wR_2 = 0.1675 for all 14090 reflections.

Crystal Data for 2: $C_{57}H_{67}B_9O_3P_3Pt_2$, M = 1380.49, monoclinic, space group $P2_1/c$, a = 14.104(6), b = 16.846(7), c = 24.842(11) Å, β = 99.021(9)°, V = 5829(4) Å^3, T = 298(2) K, Z = 4, $D_{calcd.}$ = 1.573 g/cm^3, crystal dimensions 0.45 × 0.41 × 0.29 mm, Mo-K_α radiation, λ = 0.71073 Å, R_1 = 0.0195, wR_2 = 0.0473 for 8792 reflections with $I > 2\ \sigma(I)$, and R_1 = 0.0279, wR_2 = 0.0504 for all 30174 reflections.

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