

The First Trigonal Prismatic Discrete Transition-metal Boride Cluster: Preparation and Molecular Structure of [PPN][Ru₆(H)₂(CO)₁₈B] [PPN = (Ph₃P)₂N⁺]

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The reaction of [PPN][Ru₃(CO)₉B₂H₅] with [Ru₃(CO)₁₀(NCMe)₂] leads to two borido clusters: [PPN][Ru₆(H)₂(CO)₁₈B], [PPN][1], and [PPN][Ru₆(CO)₁₇B], [PPN][2]; complex 1, the structure of which has been confirmed crystallographically, is the first example of an interstitial boron atom encapsulated within a trigonal prismatic transition-metal cage and provides a useful model for a bulk metal-rich boride.

A wide variety of clusters exhibiting an octahedral M₆C core is now known;¹ the number of related nitrido species is smaller but still significant.^{2,3} The isolation and structural characterisation of discrete transition-metal clusters, each containing a fully interstitial boron atom, has only recently been reported.^{4–10} Three of these borido clusters incorporate {AuPR₃} fragments and the M₄Au_x (M = Fe, x = 2,3; M = Ru, x = 2) framework which surrounds the boron atom is irregular.^{4,5,7} To date, fully characterised octahedral M₆B species have been restricted to [Ru₆(H)(CO)₁₇B],^{8,9} [Fe₄Rh₂(CO)₁₆B][–],^{6,10} and *mer*-[H₂Fe₃Rh₃(CO)₁₅B].¹⁰ We now report the synthesis and structural characterisation of [Ru₆(H)₂(CO)₁₈B][–] 1, which is the first example of a discrete transition-metal borido cluster displaying a trigonal prismatic cage.

Anion 1 was isolated as its [PPN] salt[†] from the reaction of [PPN][Ru₃(CO)₉B₂H₅]¹¹ with [Ru₃(CO)₁₀(NCMe)₂]. Orange [PPN][1] was collected as the third fraction in *ca.* 20% yield upon TLC separation (hexane–CH₂Cl₂, 1:1) of the crude reaction mixture. The octahedral boride [PPN][Ru₆(CO)₁₇B],⁸ [PPN][2], which was the product we had originally expected, was separated in *ca.* 10% yield from the fifth fraction. Several other products remain, as yet, uncharacterised and are the subject of current investigation. We have also isolated [PPN][1] in 5% yield from the reaction of [PPN][Ru₃(CO)₉BH₄] with [{W(η⁵-C₅H₅)(CO)₃]₂] in the presence of Me₃NO and MeCN.

A crystal of [PPN][1] suitable for X-ray diffraction analysis[‡] was grown from CH₂Cl₂ layered with hexane. The molecular structure of anion 1 is given in Fig. 1 and selected bond distances and angles are collected in the caption. The boron atom lies at the centre of a trigonal prismatic cage of ruthenium atoms, each of which carries three terminal carbonyl ligands. The Ru₆ framework is regular with ∠RuRuRu = 90 ± 2° within the square faces and ∠RuRuRu = 60 ± 2° within the triangular faces. The Ru–B distances in 1 lie in the range 2.171–2.268 Å and these values exceed those observed in the octahedral boride [Ru₆(H)(CO)₁₇B] where the range is 2.04–2.07 Å in one isomer⁸ and 2.07–2.12 Å in a second isomer.⁹ The trigonal prismatic cage confirmed for 1 is consistent with the presence of 90 valence electrons and this

necessity implies the presence of two cluster hydride ligands. These have been located directly and bridge two edges, Ru(1)–Ru(3) and Ru(4)–Ru(5), of opposing triangular faces of the prism.

The ¹¹B NMR chemical shift for [PPN][1] in CH₂Cl₂ is δ +205.9. This is close to that observed for [PPN][2], *viz.* δ +198.8 in the same solvent. (Shore *et al.*⁸ have previously reported a value of δ 196.)⁸ The close similarity between the ¹¹B NMR shifts (and thus deshielding) for a boron atoms residing in an Ru₆ octahedral or trigonal prismatic cavity contrasts with the larger deshielding experienced by a carbon or nitrogen atom in the interstice of an octahedron compared to that in a trigonal prism.^{12,13} For octahedral M₆E, the net M–E interaction is similar for E = B or C.¹⁴ This trend may be extended to E = N.^{12,13} However, while nuclear deshielding of E in the octahedral cavity is similar for E = B, C or N, in a trigonal prismatic cavity it is significantly greater for C than for N.^{12,13} Our results for E = B in 1 show a continuation of the same trend: in M₆(trigonal prism)–E, nucleus E experiences deshielding in the order B > C > N.

The structure of 1 is significant on two counts. Firstly, until this determination, the occurrence of a molecular trigonal prismatic, in preference to octahedral, M₆E cluster in which M is a group 8 metal had been confined to E = phosphorus^{15,16} although a series of trigonal prismatic carbides and nitrides of cobalt and rhodium is documented¹⁷ and this skeletal geometry is observed in the bulk state (see below). It has been tempting to consider that the preference for the trigonal prismatic Os₆ cage in [Os₆(CO)₁₈P][–] and related clusters^{15,16} is

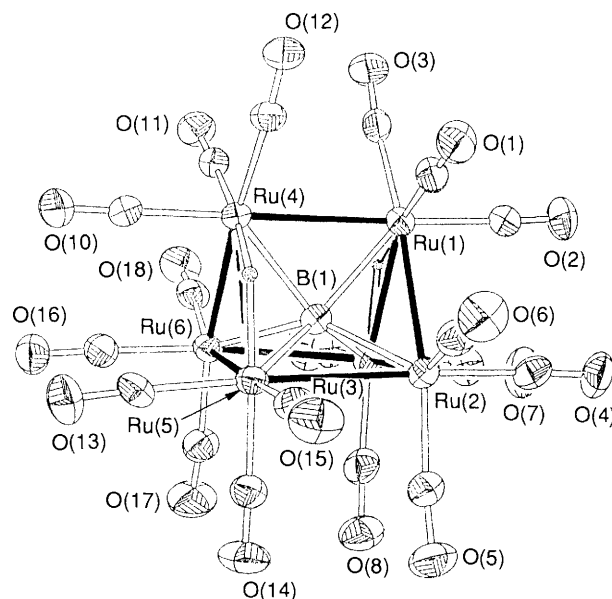


Fig. 1 Molecular structure of 1: Ru(1)–Ru(2) 2.841(1), Ru(2)–Ru(3) 2.858(1), Ru(1)–Ru(3) 2.929(1), Ru(1)–Ru(4) 2.921(1), Ru(2)–Ru(5) 2.935(1), Ru(3)–Ru(6) 2.939(1), Ru(4)–Ru(5) 2.936(1), Ru(5)–Ru(6) 2.856(1), Ru(4)–Ru(6) 2.838(1), Ru(1)–B(1) 2.247(10), Ru(2)–B(1) 2.171(8), Ru(3)–B(1) 2.208(9), Ru(4)–B(1) 2.268(8), Ru(5)–B(1) 2.204(9), Ru(6)–B(1) 2.188(10) Å

[†] [PPN][Ru₆(H)₂(CO)₁₈B], [PPN][1]: 400 MHz ¹H NMR (CD₂Cl₂) δ 7.7–7.5 (m, Ph) and –17.1 (s, Ru–H–Ru); 128 MHz ¹¹B NMR (CD₂Cl₂) δ +205.9; IR (CH₂Cl₂) ν/cm^{–1} 2042vs, 2031s, 2011w and 1987m; FAB-MS in 3-nitrobenzyl alcohol matrix, *m/z* 1066 (M[–] – 2CO) (calc. for ¹²C₁₆¹H₂¹¹B₁¹⁶O₁₆¹⁰¹Ru₆ 1067).

[‡] Crystal data for [PPN][1]: C₅₄H₃₂BNO₁₈P₂Ru₆, *M_r* = 1662.0, triclinic, *P*1, *a* = 13.459(2), *b* = 15.417(3), *c* = 15.432(2) Å, α = 109.42(1), β = 94.86(1), γ = 102.81(1)°, *U* = 2900.8(9) Å³, *Z* = 2, *D_c* = 1.903 g cm^{–3}, μ(Mo–Kα) = 16.49 cm^{–1}, *T* = 298 K. Intensity data were collected through the 2θ range of 4–52°. Of 11 019 data collected (Siemens P4 diffractometer, SHELXTL PLUS software), 10 064 were independent and 6906 with *F_o* ≥ 4.5 σ(*F_o*) were observed. Cation carbon atoms were isotropically refined owing to software limitations on number of refined parameters. *R_F* = 4.47%, *R_{wF}* = 5.69%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

a consequence of the steric requirements of the interstitial atom. However, whereas it follows that the phosphorus atom is too large for the octahedral interstice, it appears that this argument should be approached with caution. The isolation of boride **1** indicates that for first-row p-block atoms, the preference for a given group 8 M_6 cage is not driven by the size of the atom. This conclusion is consistent with observations seen previously for group 9 metals.

The second point of interest regarding the structure of **1** is its relationship to solid-state transition-metal borides. In bulk metal-rich borides containing isolated boron atoms, a common interstitial cavity is a trigonal prism.¹⁸ In particular, this is true for ruthenium, e.g. in Ru_7B_3 .¹⁹ The characterisation of **1** takes one step forward to producing transition-metal boride clusters which are realistic models for bulk metal boride materials.

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