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Macropolyhedral boron-containing cluster chemistry. The unique *nido*-five-vertex-$\langle B_2 \rangle$-*nido*-ten-vertex *conjuncto* structure of $[(\eta^5\text{-}C_5Me_5)_2Rh_2B_{11}H_{15}]$ *via* an unexpected cluster-dismantling

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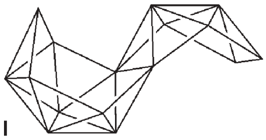
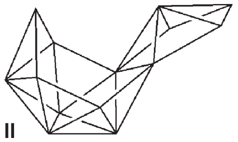
$B_{16}H_{20}$ and $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ with tmnd give $[(\eta^5\text{-}C_5Me_5)_2Rh_2B_{11}H_{15}]$, which has an unprecedented thirteen-vertex macropolyhedral cluster core based on a *nido* ten-vertex $\{MB_9\}$ subcluster and a *nido* five-vertex $\{MB_4\}$ subcluster fused with their open-face $\{B_2\}$ edges in common.

One method of extending contiguous polyhedral boron containing cluster chemistry beyond the barrier of the stable twelve-vertex icosahedron is by the expansion of the icosahedron by the insertion of additional vertices, and this twelve-vertex hiatus has so been crossed to attain species with thirteen, fourteen and fifteen vertices.[1,2] A second method of extension is by the intimate fusion of smaller cluster units together to form contiguous 'macropolyhedral' multicluster assemblies in which the clusters are linked by two or more cluster atoms held in common;[3–5] thence cluster Aufbau on such macropolyhedral species can increase the numbers of vertices further.[6] Using these latter approaches, there are many examples of macropolyhedral species of seventeen or more vertices,[5,7,8] but characterised smaller macropolyhedrals of between thirteen and seventeen vertices are very rare. The two best known examples are $B_{16}H_{20}$ **1** and $B_{14}H_{18}$ **2**,[9,10] which consist structurally of *nido* ten-vertex $\{B_{10}\}$ subclusters fused, with a common $\{B_2\}$ edge, to *nido* eight-vertex $\{B_8\}$ and *nido* six-vertex $\{B_6\}$ clusters respectively (schematics **I** and **II** respectively).



I



II

We now report an unprecedented example of *nido* ten-vertex and *nido* five-vertex subclusters fused with a common $\{B_2\}$ edge (basic skeletal type **III A**) to give a thirteen-vertex macropolyhedral. This new architecture occurs in the dimetallaborane species $[(\eta^5\text{-}C_5Me_5)_2Rh_2B_{11}H_{15}]$ **3** (Fig. 1), which has *nido* ten-vertex $\{MB_9\}$ and *nido* five-vertex $\{MB_4\}$ subclusters so fused, and which has the $\{Rh(\eta^5\text{-}C_5Me_5)\}$ metal centres M positioned as in schematic **III B**. The compound is the product of an unexpected cluster dismantling in the reaction between $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ and $B_{16}H_{20}$ in the presence of the non-nucleophilic base *N*,*N*,*N′*,*N′*-tetramethylnaphthalene-1,8-diamine (tmnd). It is formally a model of the long-predicted but as yet unknown binary borane $B_{13}H_{17}$, which would be a member of the $\{nido{:}\langle B_2 \rangle{:}nido\}$ macropolyhedral $\{B_nH_{n+4}\}$ family that includes the better examined $B_{18}H_{22}$ isomers as well as $B_{16}H_{20}$ **1** and $B_{14}H_{18}$ **2** mentioned above.

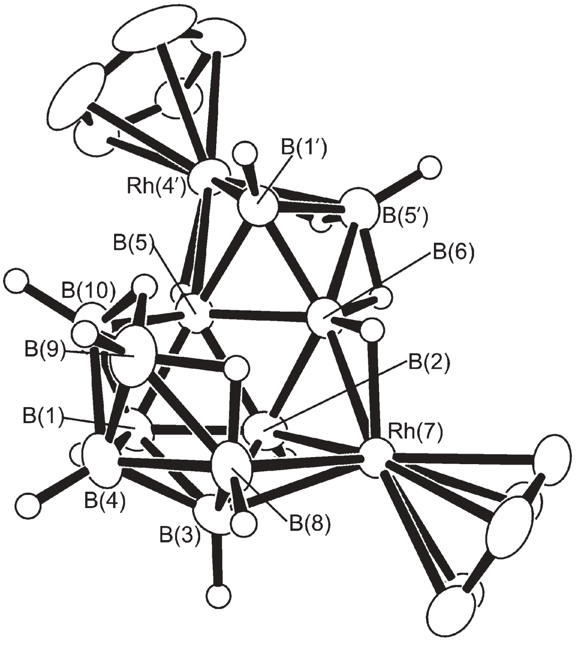


Fig. 1 Crystallographically determined molecular structure for $[(\eta^5\text{-}C_5Me_5)_2Rh_2B_{11}H_{15}]$ **3**,[11] with C-methyl groups omitted for simplicity. Compound **3** crystallised from $CDCl_3$–C_6H_{14} with a 17% occupancy of the {BH(5′)} site by {BCl}. Anisotropically determined atom positions are defined with 50% probability ellipsoids. Selected interatomic distances are as follows: Rh(7) to B(2) 2.198(3), B(3) 2.199(3), B(6) 2.182(3), B(8) 2.240(3) and to C(cyclopentadienyl) 2.200(3)–2.231(2) Å; Rh(4′) to B(1′) 2.108(3), B(5) 2.326(3), B(5′) 2.264(3) and to C(cyclopentadienyl) 2.150(3)–2.243(3) Å. Interboron distances are in the range 1.714(6) for B(4)–B(9) to 1.888(4) Å for B(5)–B(10), selected other values being B(5)–B(6) 1.780(4), B(5′)–B(6) 1.797(5), B(8)–B(9) 1.816(5) and B(9)–B(10) 1.803(5) Å.

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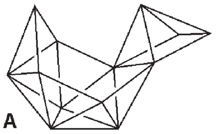
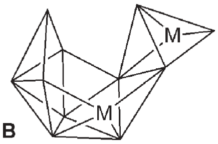
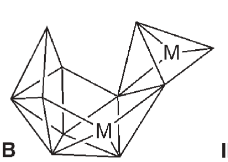


III A

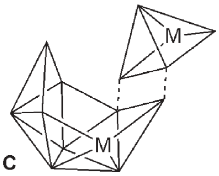


III B

Thus, a solution of $B_{16}H_{20}$ **1** (20 mg; 100 μmol), tmnd (45 mg; 210 μmol) and $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ (65 mg; 110 μmol) in dichloromethane (*ca.* 15 ml) was stirred at room temperature for 48 h under an atmosphere of dry nitrogen. Filtration through flash silica, followed by reduction in volume *in vacuo* and preparative TLC (silica-gel G, Fluka GF_{254}; dichloromethane–*n*-hexane, 50 : 50 vol/vol) revealed several coloured products. Four principal components were apparent: yellow **5** (R_F 0.62), pink **7** (R_F 0.52), orange **3** (R_F 0.46); and red-purple **4** (R_F 0.36). Components **3**, **4** and **5** were purified by repeated preparative TLC, but **7** could not be sufficiently purified for characterisation. Orange **3** was identified *via* single-crystal X-ray diffraction studies[11] and NMR spectroscopy[12] as 4′,7-bis(η^5-pentamethylcyclopentadienyl)-*nido*-4′-rhodapentaborano-+2′,3′:5,6-*nido*-7-rhodadecaborane, $[(\eta^5\text{-}C_5Me_5)_2Rh_2B_{11}H_{15}]$ (21 mg; 34 μmol; 33%). Because obtainable crystals of compound **3** were small, the use of a synchrotron radiation source was necessary to obtain sufficient X-ray diffraction data for analysis. Red-purple **4** was identified *via* single-crystal X-ray diffraction studies[11] and NMR spectroscopy[12] as $[9,7'\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}9,7'\text{-}Rh_2B_{16}H_{19}\text{-}2'\text{-}Cl]$ **3** (22 mg; 31 μmol; 30%; schematic **IV**), a direct analogue of the recently reported iridium species $[9,7'\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}9,7'\text{-}Ir_2B_{16}H_{17}\text{-}2'\text{-}Cl]$,[13] formed by a combination of metal-centre addition and boron-frame rearrangement. Yellow **5** was identified *via* NMR spectroscopy[12] and single-crystal X-ray diffraction[11] as $[5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}\textit{nido}\text{-}5\text{-}RhB_9H_{13}]$ (6 mg; 17 μmol; 16%; schematic **V**), also previously reported.[14]

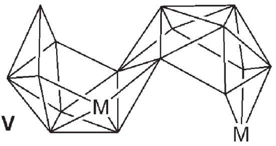


III B

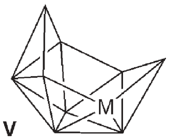


III C

As mentioned above, the structure of compound **3** can be factorised into ten-vertex *nido* $\{MB_9\}$ and five-vertex *nido* $\{MB_4\}$ subclusters that are fused with two boron atoms held in common (schematic **III C**). The larger subcluster is formally of ten-vertex *nido*-5-metalladecaborane constitution, for which there is ample precedent in single-cluster compounds, *e.g.* as in $[5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}5\text{-}\textit{nido}\text{-}RhB_9H_{13}]$ **5** (also a product of this reaction, schematic **V**) and as in one of the first reported examples, $[5\text{-}(\eta^5\text{-}C_5H_5)\text{-}5\text{-}\textit{nido}\text{-}CoB_9H_{13}]$.[15] [Note that IUPAC numbering convention often dictates a different numbering for the macropolyhedral subclusters as compared to their single cluster analogues.] The smaller subcluster is of five-vertex *nido*-2-metallapentaborane constitution, *e.g.* again as in one of the first examples reported, $[1\text{-}(C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}CoB_4H_8]$.[15] In compound **3** the novelty resides *(a)* in the first experimental instance of these two well-recognised structural types being fused together, long elusive, and *(b)* in its formation in the relatively high yield of 33%, which augurs well for the exploration of this type of system to give still higher yields and on a larger scale suitable for construction of further novel macropolyhedral frameworks.



IV



V

As we have recently reported elsewhere,[13,16,17] the $B_{16}H_{20}$ substrate in its reactions with metal centres can engender novel molecular geometries and other novel metallaborane cluster features *(a)* by cluster-*Aufbau* processes as well as *(b)* by a combination of cluster-*Aufbau* allied with unexpected cluster-rearrangements. The latter combination is also apparent in this present reaction system, in the formation of compound **4**. The observation here of a third process, *viz.* *(c)* cluster-dismantling by loss of boron vertices, presaging a potential for the generation of additional families with further unanticipated structural novelty, adds further merit to the continuing investigation of the products from the reaction of $B_{16}H_{20}$ with metal complexes. In particular, the generation here of $\{MB_9\}$ and $\{M_2B_{11}\}$ as well as $\{M_2B_{16}\}$ frameworks augurs excellently for the isolation of macropolyhedrals with one or more metal centres and fewer than sixteen boron atoms for the establishment of the structural paradigms in the elusive and sparsely represented twelve-vertex-to-seventeen-vertex macropolyhedral region.

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11 Crystallographic data; Compound **3**: $C_{20}H_{44.83}B_{11}Cl_{0.17}Rh_2$: M = 616.15, triclinic (0.08 × 0.02 × 0.02 mm, orange-red rod from $CDCl_3$–hexane), space group $P\bar{1}$, a = 8.8255(5), b = 9.9185(6), c = 17.9003(10) Å, α = 89.867(1), β = 79.475(1)°, γ = 68.194(1)°, U = 1426.63(14) $Å^3$, D_{calc} = 1.434 Mg m^{-3}, Z = 2, λ = 0.6932 Å [synchrotron wiggler-generated radiation (R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, I. Burrows, D. J. Taylor, S. J. Teat and M. Hamichi, *J. Synchrotron Radiat.*, 1997, **4**, 279; R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, I. Burrows, D. J. Taylor, S. J. Teat and M. Hamichi, *J. Synchrotron Radiat.*, 2000, **7**, 40; J. Bould, W. Clegg, J. D. Kennedy, S. J. Teat and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1997, 2005; W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1998, 3037)], μ = 1.181 mm^{-1}, T = 150(2) K, R_1 = 0.0353 for 6095 reflections with $I > 2\sigma(I)$, and wR_2 = 0.097 for all 7239 independent reflections; CCDC 644825. Compound **4**: $C_{20}H_{49}B_{16}ClRh_2$: M = 703.82, monoclinic (0.69 × 0.43 × 0.40 mm, dark red block from $CDCl_3$–hexane), space group Pc, a = 11.4055(2), b = 10.4608(2), c = 14.3232(3) Å, β = 109.5450(10)°, U = 1610.44((5) $Å^3$, D_{calc} = 1.451 Mg m^{-3}, Z = 2, λ = 0.71073 Å (Mo-Kα), μ = 1.121 mm^{-1}, T = 150(2) K, R_1 = 0.033 for 5940 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0.0849 for all 5977 independent reflections; CCDC 644826. Methods and programs were standard (G. M. Sheldrick, *SHELX97*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXTL Manual*, Bruker AXS Inc., Madison, WI, USA, 1994 and 1998; L. J. Farrugia, ORTEP-3, *J. Appl. Crystallogr.*, 1997, **30**, 565). Obtained crystals of compound **5** from $CDCl_3$–hexane were orthorhombic, space group $Pnma$, a = 11.02189(5), b = 9.9185(6), c = 17.9003(10) Å U = 1718.85(14) $Å^3$, D_{calc} = 1.347 Mg m^{-3}, at T = 150(2), Z = 4; however, disorder across the plane containing Rh(5), B(7) and B(8), which is a crystallographic mirror plane (but only a pseudo mirror plane for the molecule), precluded good location of all atomic positions; CCDC 644826. CCDC 644825–644827. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709470a.

12 Cluster NMR data, 300 K, ordered as: tentative assignment $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm of directly bound H atoms]; assignments by $\{^{11}B–^{11}B\}$ and $^{1}H–\{^{11}B\}$ correlation spectroscopy. $\{Rh_2B_{11}\}$ compound **3**, CD_2Cl_2: B(6) +15.6 [*conjunto* position, no directly bound H(*exo*)], BH(8) +13.9 [+2.12], BH(3) +5.5 [+3.22], BH(1′) +2.1 [+3.31], B(2) −1.9 [+1.25], BH(10) −4.0 [+1.34], BH(5′) −10.9 [+2.26], BH(9) −13.0 [+2.54] and B(5) −25.1 [*conjunto* position, no directly bound H(*exo*)], BH(4) −42.9 [−0.08], with $\delta(^{1}H)$/ppm for (μ-H)(4′,5) −9.23 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 30 Hz)], (μ-H)(4′,5′) −9.56 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 30 Hz)], (μ-H)(5′,6) −0.91, (μ-H) (6,7) −10.14 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 30 Hz)], (μ-H) (8,9) −0.97 and (μ-H) (9,10) −2.11, and for $\{C_5Me_5\}$ +1.97 and +1.98. $\{Rh_2B_{16}\}$ compound **4**, CD_2Cl_2 (compare $\{Ir_2\}$ analogue, ref. 13): BH(8) +23.2 [+4.38], BH(8′) +22.1 [+4.00], BH(10′) *ca.* +14.0 [+4.30], BH(1) *ca.* +14.0 [+3.82], BH(10) *ca.* +9.7 [+3.43] BH(5) *ca.* +9.7 [+3.33], B(7) +7.3 [*conjunto* position, no directly bound H(*exo*)], B(6) −0.5 [*conjunto* position, no directly bound H(*exo*)], BH(1′) −0.2 [+2.61], B(2′) −0.2 [bound to Cl(*exo*)], BH(3) *ca.* −3.6 [+3.10], BH(9′) *ca.* −3.6 [+2.34], BH(3′) −5.8 [+2.79], BH(4) −6.8 [+1.18], BH(2) −21.0 [+0.48] and BH(4′) −40.1 [+0.41]; with $\delta(^{1}H)$/ppm for (μ-H)(9′,10′) −0.15, (μ-H)(8′,9′) −2.61, (μ-H)(5,6) −2.47, (μ-H)(9,10) −7.65 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 30 Hz)], (μ-H)(8,9) −7.94 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 30 Hz)] and (μ-H)(7,7′) −11.46 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 30 Hz)], and for $\{C_5Me_5\}$ +1.98 and +2.03. $\{RhB_9\}$ compound **5**, $CDCl_3$ (compare ref. 12): BH(6) +28.9 [+4.54], BH(1) +25.8 [+3.93], BH(3) +9.8 [+2.86], BH(8) +5.4 [+3.10], BH(7) +2.5 [+2.71], BH(9) +0.8 [+3.17], BH(10) +0.9 [+2.32], BH(2) −13.0 [+0.75] and BH(4) −28.1 [+0.35]; with $\delta(^{1}H)$/ppm for (μ-H)(5,6) −12.68 [$^{1}J(^{103}Rh–^{1}H)$ *ca.* 35 Hz)], (μ-H)(6,7) −2.48, (μ-H)(8,9) −2.77, (μ-H)(9,10) −1.91 and $\{C_5Me_5\}$ +1.87.

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