nido-$[\{(C_5Me_5)Ir\}B_3H_7\{(PPh_3)_2(CO)Os\}]$, *closo*-$[\{(C_5Me_5)Ir\}B_4H_6\{(PPh_3)_2(CO)Os\}]$ and *pileo*-$[\{(PPh_3)COHIr\}B_5H_5\{(PPh_3)_2(CO)Os\}]$: a Unique Homologous Series of Iridaosmaborane Cluster Types

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The synthesis and characterization of *nido*-$[\{(C_5Me_5)Ir\}B_3H_7\{(PPh_3)_2(CO)Os\}]$, *closo*-$[\{(C_5Me_5)Ir\}B_4H_6\{(PPh_3)_2(CO)Os\}]$ and *pileo*-$[\{(PPh_3)COHIr\}B_5H_5\{(PPh_3)_2(CO)Os\}]$, a unique series of iridaosmaborane clusters containing three, four and five boron atoms, respectively, are reported.

We are interested in the preparation of homo- and hetero-polymetallaboranes based on small borane templates containing 5–7 vertices. Our approach is to add metal moieties to metallaboranes rather than to build the cluster from a metal complex and a tetrahydroborate or monoborane adduct. The latter methods have seen much success recently in the laboratories of Leach, Housecroft and Fehlner and their respective coworkers[1] but they are not suited to the formation of heterobimetallaboranes. Indeed, there are few examples of heteropolymetallaboranes in the literature containing 5–7 vertices.[2] The first *nido* species to be prepared was $Cu(Ph_3P)_2B_5H_8Fe(CO)_3$,[3a] a bimetallaborane in which the Fe is a true vertex and the Cu group may be considered as a 'pseudo-proton'. The osmaplatinaheptaboranes $[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]$ and $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$,[3b] discovered a little later, and the recently reported related *nido*-$(PPh_3)_2(CO)HIr(PMe_2Ph)ClPtB_5H_6$[3c] may be considered to be true heterobimetallaboranes in that both metals are vertices. Finally there is $Cu(Ph_3P)_2B_6H_9Fe(CO)_4$,[3d] prepared in our laboratory, in which both metals are pseudo-protons in that they occupy positions which may be formally replaced by protons. Grimes and coworkers described the first example of a *closo*-heteropolymetallaborane in this context, *closo*-$[(C_5H_5)_2Co_2(CO)_4FeB_3H_3]$,[4a] which contains a trimetal triangle and quite recently we reported the species *closo*-$[(PPh_3)(CO)_2IrB_5H_4(PPh_3)Fe(CO)_3]$,[4b] the first structurally characterized *closo*-heterobimetallaheptaborane. Most recently the novel species *pileo*-$[\{(C_5H_5)Fe\}(ML_3H)B_5H_7]$ (M = Mo, L = PMe_2Ph, **4a**; M = W, L = PMe_3, **4b**)[5] were reported from use of a similar synthetic approach to that described herein. Here we extend the range of heterobimetallaboranes by describing the formation and characterization of a unique homologous series of iridaosmaboranes based on reactions of the substrate $[(PPh_3)_2(CO)OsB_5H_9]$.[6a] This series consists of clusters based on a *nido* square pyramid, a *closo* octahedron and a *pileo* capped octahedron,[7] the basic cluster skeletons all differing formally by the presence of one BH vertex.

$[\{(PPh_3)(CO)HIr\}B_5H_5\{(PPh_3)_2(CO)Os\}]$, **1**, is prepared by the treatment of a solution of $Li[(PPh_3)_2(CO)OsB_5H_8]$, prepared at −35 °C from $[(PPh_3)_2(CO)OsB_5H_9]$ and MeLi in THF, with *trans*-$[(PPh_3)_2(CO)IrCl]$. It is isolated as the principal bimetallaborane product as a pale yellow solid in 33% yield, along with the known species $[(PPh_3)_2(CO)OsB_4H_8]$.[6a] If Bu^{n}Li is used in the preparation, a derivative of the latter, $[(PPh_3)_2(CO)OsB_4H_7(C_4H_9)]$,[6b] is formed in 14% yield. Spectral data identified **1** as *pileo*-$[\{(PPh_3)(CO)HIr\}B_5H_5\{(PPh_3)_2(CO)Os\}]$.†[7] This was confirmed by a single crystal structure determination.‡ The structure of **1**, Fig. 1(*a*), consists of an $IrOsB_4$ octahedron with a BH group capping the IrOsB face. As such it represents only the third fully characterized example of a BH group capping a BMM′ triangular face. The other examples are the recently reported *pileo*-$[\{(C_5H_5)Fe\}B_5H_7(ML_3H)]$, **4a,b**, mentioned above, in which the BH vertex caps a BFeM′ face. Related to these systems is $[(\eta^5\text{-}C_5Me_5)_2Ir_2B_5H_5]$ **5**, in which the BH group caps a BIrIr face.[8] The H atom on the Ir in **1** was identified by NMR spectroscopy.

Treatment of a solution of $Li[(PPh_3)_2(CO)OsB_5H_8]$ with $[(C_5Me_5)IrCl_2]_2$ results in the formation of a clear red–brown solution. The principal products were two yellow solids **2** and **3**, obtained after chromatographic separation on silica gel using 50 : 50 CH_2Cl_2–C_5H_{12}. Compound **2** was identified as *closo*-$[\{(C_5Me_5)Ir\}B_4H_6\{(PPh_3)_2(CO)Os\}]$ by NMR, IR and MS data, and by elemental analysis on the CH_2Cl_2 solvate, and was obtained in up to 21% yield.† Crystals solvated with C_6H_6 were amenable to a single crystal X-ray analysis which gives the structure indicated in Fig. 1(*b*).‡ Compound **2** consists of a 4 : 1 mixture of $[\{(C_5Me_5)Ir\}B_4H_6\{(PPh_3)_2(CO)Os\}]$ and the 4-Cl derivative. It exists as a an $IrOsB_4$ octahedron with four terminal and two bridging H atoms. Thus it is analogous to the species $[\{(C_5H_5)Co\}_2B_4H_6]$ and its (C_5Me_5) analogue.[9] NMR spectra and the X-ray structure determination of **2** suggest that there are

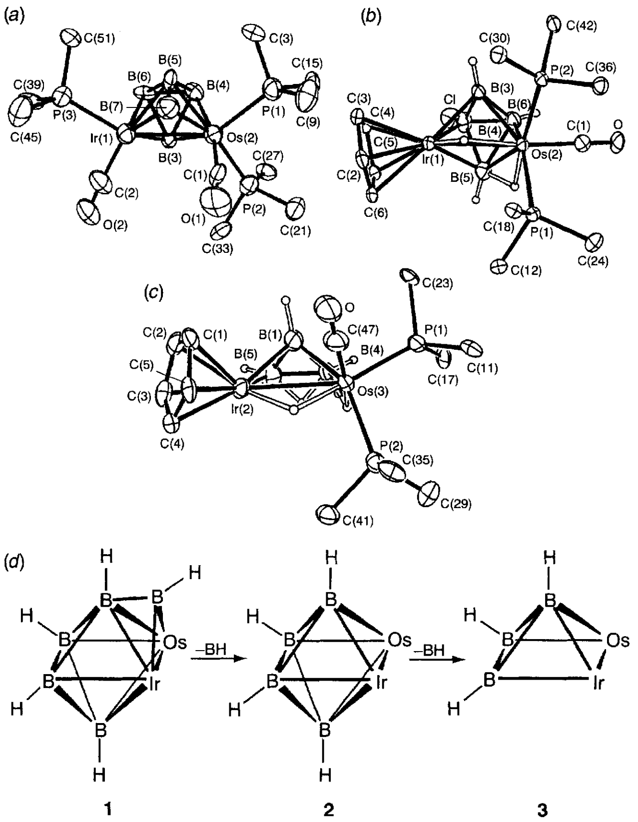

Fig. 1 Projection views of (*a*) *pileo*-$[\{(PPh_3)(CO)HIr\}B_5H_5\{Os(PPh_3)_2(CO)\}]$, **1**; (*b*) *closo*-$[\{(C_5Me_5)Ir\}B_4H_5Cl\{(PPh_3)_2(CO)Os\}]$ **2**; and (*c*) *nido*-$[\{(C_5Me_5)Ir\}\{(PPh_3)_2(CO)Os\}B_3H_7]$ **3**, showing only the *ipso*-C atoms of the phenyl groups and with the methyl groups omitted for clarity. In addition to a terminal H atom on each B there is a terminal H on Ir(1) in **1**, as indicated by ^1H NMR spectra. The assignment of the relative positions of the Os and Ir atoms is uncertain and may be reversed. Also, in **3** there is a μ-H atom bridging Ir(2) and B(5). (*d*) Sequential removal of B–H vertices from a *pileo* cluster type **1** giving cluster types **2** and **3**.

two μ-H atoms on the Ir(1)–Os(2)–B face pointing towards the 'missing' *pileo* capping vertex of **1**. At 25 °C, both ^{11}B and ^{1}H NMR spectra indicate exchange of μ-H atoms and the BH vertices at positions 3 and 5. Compound **2** is the first example of a structurally characterized *closo*-metallaborane containing two cage edge-bridging H atoms; one example with a single bridging H exists for a *closo*-B_{10} system[10] and the *pileo*-systems **4**, described very recently by Leach and coworkers,[5] also contain two μ-H atoms. Compound **3** was obtained in 4.5% yield and identified as $[\{(C_5Me_5)Ir\}B_3H_7\{(PPh_3)_2(CO)Os\}]$ by NMR, IR, MS and a single crystal X-ray structure determination [Fig. 1(*c*)].†‡ It exists as a bimetallapentaborane(9) species with the metal atoms in the 2,3 positions and is related to **2** by the removal of a BH vertex at position 3 or 5 in the latter. Compound **3** is the first example of a bimetallapentaborane(9) with the metal atoms in adjacent basal positions and it is the first heterobimetallapentaborane(9) to be reported.

The species **1–3** represent a novel series of heterobimetallaboranes. Compound **1** conforms to the polyhedral skeletal electron pair theory (PSEPT) for a capped-closed octahedron containing 14 skeletal electrons and seven vertices.[11] Removal of B–H vertices from this *pileo* cluster sequentially is illustrated in Fig. 1(*d*). As predicted by the PSEPT,[12] formal removal of one B–H vertex from **1** leads to the formation of the 14 skeletal electron *closo*-cluster **2** containing 6 vertices, and removal of a second B–H vertex leads to the formation of the conventional 14 skeletal electron 5-vertex *nido*-cluster **3**. In the case of both **2** and **3**, bridging H atoms sit on a face from which a vertex has been removed and point towards the missing vertex or vertices. Formation of **1** by insertion of the $[(PPh_3)_2(CO)Ir]^+$ moiety into the $[OsB_5]^-$ cluster is clearly a complex process not easily explained, but it is noteworthy that the addition of a metal reagent to a *nido*-FeB_5, described in ref. 5, forms **4a** and **4b**, species which are also capped octahedral clusters. The evidence suggests that *pileo* species may be the preferred closed structures in 7-vertex bimetallaborane clusters. Formations of **2** and **3** are also not easily explained but it is known that MB_5 clusters tend to degrade to smaller clusters,[13*a*] an observation which is suggested by theory.[13*b*] Our results suggest that **3** formed from **2**, so the idea of sequential loss of vertices in such series of clusters is not unreasonable. Clearly there is much chemistry to be explored here and we expect to report on some of it in the near future.

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Footnotes

† *Physical data* for **1**: ^{11}B (160.5 MHz), ^{1}H (500.1 MHz) and ^{31}P (122 MHz) NMR ($CDCl_3$, 25 °C): $\delta_{^{11}B}$ 94 (1B), 77.2 (1B), 71.5 (1B), 56.8 (1B), −7.5 (1B); $\delta_{^{1}H}$ 10.59, 10.33, 10.15 (*J* 17.8 Hz), 7.80 (*J* 12.0 Hz), −4.03, −8.29 (*J* 15.5 Hz); $\delta_{^{31}P}$ +7.86 ($^{2}J_{^{31}P_A,^{31}P_C}$ 13 Hz, P_A), +6.99 ($^{2}J_{^{31}P_B,^{31}P_C}$ 24 Hz, P_B), +0.96 ($^{2}J_{^{31}P_C,^{31}P_A}$ 13 Hz, P_C); IR ν_{max}/cm^{-1} 2528 m (BH), 2000 s (CO on Ir), 1941 (CO on Os); LR FABMS *m*/*z* 1285 [P^+(100%), calc for $C_{56}H_{51}B_5O_2P_3IrOs$, 1285.28]. For **2**: NMR $\delta_{^{11}B}$ 25 °C: 55.7 (1B), 45.7 (1B), 23.9 (2B); −94 °C: 54.7 (1B), 43.0 (1B), 35.4 (1B), 6.7 (1B); $\delta_{^{1}H}$ 25 °C: 10.03 (1H), 9.18 (1H), 3.98 (2H), −15.27 (2H), 1.74 (15H); −94 °C: 10.02 (1H), 9.20 (1H), 5.19 (1H), 2.59 (1H), −11.65 (1H), −19.20 (1H), +1.65 (15H); $\delta_{^{31}P}$ 25 °C: −6.24 (s); −89 °C ($CD_3C_6D_5$): −5.53 (s); IR ν/cm^{-1} 2497 m, 2425 sh (BH), 1950 (CO); Electrospray HRMS: *m*/*z* 1120.295 [P^+(100%), calc. for $^{12}C_{47}{}^{1}H_{51}{}^{11}B_4{}^{16}O^{31}P_2{}^{193}Ir^{192}Os$, 1120.305]. For **3**: NMR $\delta_{^{11}B}$ 25 °C: 19.8 (1B), 14.5 (2B); $\delta_{^{1}H}$ 6.9 (1H), 6.78 (1H), 2.48 (1H), −0.80 (B–H–B), −8.81 (Os–H–B), −16.20 (Ir–H–B), −17.73 (Ir–H–Os), $^{2}J_{^{31}P_{A/B}{}^{1}H_{cis}}$ 19 Hz, $^{2}J_{^{31}P_{B/A}{}^{1}H_{trans}}$ 29 Hz, 1.79 (15); $\delta_{^{31}P}$ +19.4 (P_A), −1.4 (P_B), ($^{2}J_{^{31}P,^{31}P}$ 9.6 Hz); IR ν/cm^{-1} 2500 m (BH), 1925 s (CO); LRMS (FAB) *m*/*z* 1110.3 [P^+(100) calc. for $C_{47}H_{52}B_3OP_2IrOs$, 1110.30].

‡ *Crystal data*: $C_{58}H_{53}B_5Cl_6O_2P_3IrOs$ **1**: T = 295(2) K, a = 16.955(5), b = 13.790(6), c = 25.915(6) Å, β = 94.28(2)°, V = 6042(4) Å^3, Z = 4, space group $P2_1/c$, μ = 4.687 mm^{-1}. D_c = 1.674 g cm^{-3}. For $C_{53}H_{56.80}Cl_{0.20}B_4OP_2IrOs$ **2**: T = 140(2) K, a = 11.112(3), b = 12.765(4), c = 18.323(5) Å, α = 76.48(2), β = 72.71(2), γ = 83.73(2)°, V = 2410.6(12) Å^3, Z = 2, space group $P\bar{1}$, μ = 5.506 mm^{-1}, D_c = 1.659 g cm^{-3}. For $C_{47}H_{52}B_3OP_2IrOs$ **3**: T = 293(2) K, a = 31.305(5), b = 31.503(5), c = 25.386(5) Å, V = 21819(6) Å^3, Z = 18, space group $R\bar{3}$, μ = 5.463 mm^{-1}, D_c = 1.627 g cm^{-3}. Of 16701, 13392 and 15602 reflections collected, 15076, 12758 and 9370 independent used in refinement for **1**, **2** and **3**, respectively. Data collected on a Siemens R3 automated diffractometer using ω–2θ scans with variable scan speed. Data reduction and structure solutions carried out using SHELXTL-PLUS (VMS) (G. M. Sheldrick, 1991, Siemens Analytical X-Ray Division, Madison, WI). Least-squares refinements were achieved using SHELXL-93 (G. M. Sheldrick, 1993, SHELXL-93 structure refinement package, Universität Göttingen, Germany). Full-matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The final residual values were $R(F)$ = 9.92, 4.40 and 6.94% for reflections $I > 2\,\sigma(I)$, $wR(F^2)$ = 24.44, 10.14, 17.12%, s = 1.010, 1.068 and 1.033, number of parameters = 778, 573, 504 for **1**, **2** and **3**, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters for **1–3** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J. Bullick, P. D. Grebenik, M. L. H. Green, A. K. Hughes, J. B. Leach and P. C. McGowan, *J. Chem. Soc., Dalton Trans.*, 1995, 67; C. E. Housecroft, D. M. Matthews and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1992, 323; Y. N. Nishihara, K. J. Deck, M. Shang, T. P. Fehlner, B. S. Hagerty and A. L. Rheingold, *Organometallics*, 1994, **13**, 4510.

2 J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; 1986, **36**, 211; K. B. Gilbert, S. K. Boocock and S. G. Shore, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, E. W. Abel and F. G. A. Stone, Pergamon, Oxford, 1982, Part 6, ch. 41, pp. 879–945; L. Barton and D. K. Srivastava, *Comprehensive Organometallic Chemistry, II*, ed. G. Wilkinson, E. W. Abel and F. G. A. Stone, Pergamon, Oxford, 1995, in the press.

3 (*a*) M. Mangion, J. D. Ragaini, T. A. Schmitkons and S. G. Shore, *J. Am. Chem. Soc.* 1979, **101**, 754; (*b*) J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1991, 185; (*c*) J. Bould and L. Barton, *Abstracts, Fourth Boron-USA Workshop*, Syracuse, NY, July, 1994, No. 45; (*d*) L. Barton and D. K. Srivastava, *Organometallics*, 1991, **10**, 2982.

4 (*a*) R. Weiss, J. R. Bowser and R. N. Grimes, *Inorg. Chem.*, 1978, **17**, 1522; (*b*) J. Bould, N. P. Rath and L. Barton, *Angew. Chem.*, in the press.

5 J. Bullick, P. D. Grebenik, M. L. H. Green, A. K. Hughes, J. B. Leach and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1994, 3337.

6 (*a*) J. Bould, N. N. Greenwood and J. D. Kennedy, *J. Organomet. Chem.*, 1983, **249**, 11; (*b*) J. Bould, N. P. Rath and L. Barton, to be published.

7 For a definition of *pileo*, see: J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 523.

8 J. Bould, N. P. Rath and L. Barton, *Organometallics*, 1995, **14**, 2119.

9 V. R. Miller, R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, 1977, **99**, 5646; T. L. Venable and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 887.

10 This is the species $[1,1\text{-}(PMe_2Ph)_2\text{-}1,2\text{-}\mu\text{-}H\text{-}2,5\text{-}(OMe)_2$-*isocloso*-$1\text{-}RhB_{10}H_8]$; H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 517.

11 D. M. P. Mingos and M. I. Forsyth, *J. Chem. Soc., Dalton Trans.*, 1977, 610.

12 R. E. Williams, *Inorg. Chem.*, 1971, 10, 210; K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1971, **18**, 1; D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311.

13 (*a*) Unpublished observations from our laboratory; (*b*) A. M. Mebel, K. Morokuma and D. G. Musaev, *J. Am. Chem. Soc.*, 1994, **116**, 3932.